POLYMORPHIC TRANSITIONS OF 35 SUBSTANCES TO 50,000 Kg/Cm²

BY P. W. BRIDGMAN

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CONTENTS

Introduction

In a previous paper I have briefly described a new form of high
pressure apparatus with which pressures up to 50000 kg/cm^2 may be
reached,[1] and I also described the polymorphic transitions of the ele-
ments which had been studied with this apparatus.   In this present
paper the thermodynamic parameters of the transitions of a number
of inorganic compounds are given, and also a detailed discussion of a
number of matters of technique connected with the new apparatus
for which there was no room in the preceding paper.

Details of Technique

The general scheme of the apparatus is suggested by Figure 1,
reproduced from the previous paper.   The "cylinder" A in which

Figure 1.   Schematic representation of method of automatically subject-
ing the pressure vessel to external pressure.

pressure is produced has a conical external surface, like a stopper.
Pressure is produced in this "stopper" by means of the piston P.
The thrust exerted on the stopper by the piston is taken up by the
conical collar into which the stopper fits, and which exerts an external
pressure on the stopper proportional to the total thrust, neglecting
friction.

The magnitude of the external pressure on the stopper can be readily calculated. If T is the total thrust exerted by the piston and

FIGURE 2.   Diagram for calculating relation between thrust and external pressure.

p the pressure per unit area exerted by the collar, then to a sufficient approximation, for small angles of the cone: (see Figure 2)

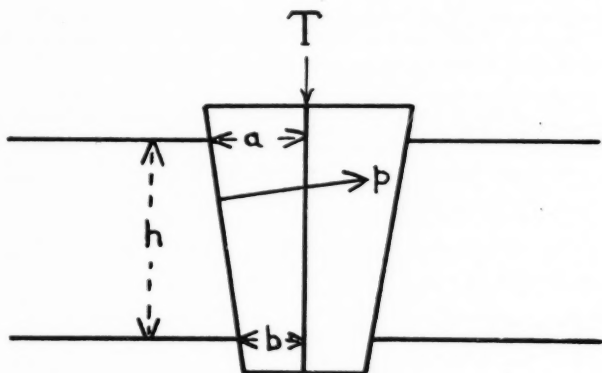$$T = p \, \frac{a - b}{h} . \; h2\pi \, \frac{a + b}{2},$$

or

$$p = \frac{T}{\pi (a^2 - b^2)}$$

That is, the pressure exerted by the collar is equal to that which would be produced by the total thrust on the piston concentrated on the annulus corresponding to the difference between the two ends of the cone. In the actual apparatus, $h = 1$ inch, $a = 0.516$ inches, and the taper was 1.25 inches per foot (double angle). This makes the area of the annulus 0.160 square inches. The usual diameter of the piston was 0.265 inches, area 0.0552 square inches, so that a pressure on the piston of 50,000 kg/cm² produces an external pressure on the stopper of $\frac{.0552}{.160} \times 50,000$ or 17,200 kg/cm².

The collar supporting the stopper was made of the same material as most of my previous high pressure cylinders, chrome vanadium

steel, and heat treated in the regular way. The collar was seasoned
by a preliminary stretching, by forcing into it a cone, until a perma-
nent set of perhaps 5 per cent was produced. It was then ground to
final dimensions. The pressure of approximately 17000 in the collar
was as high as I felt could be comfortably used in this grade of steel.
It would be possible to somewhat improve on these figures by the
use of "Solar" steel, using a somewhat smaller angle for the stopper,
and I shall do this when I have a chance to reconstruct the apparatus.

The friction between stopper and collar is a very important matter,
and unless precautions are taken, may be so great as to seriously
diminish the effectiveness of the external support. The friction may
be conveniently evaluated by measuring the distance the stopper is
pushed into the collar as a function of the total thrust, with increasing
and decreasing thrust. A cyclic curve of the general shape of Figure 3

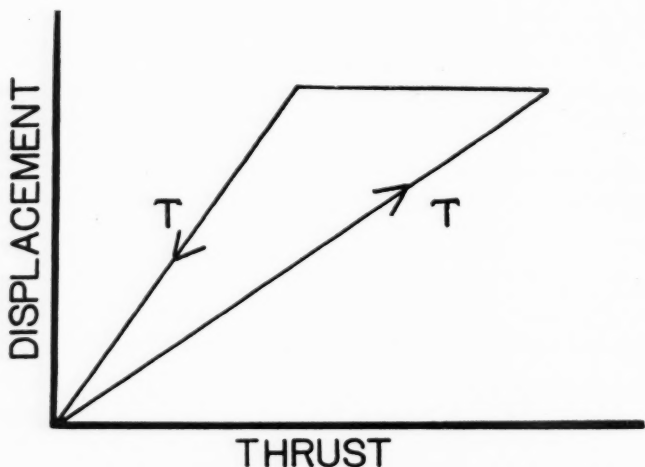FIGURE 3. The cyclic relation between thrust and displacement of the
stopper into its sleeve.

will be obtained. The difference between ascending and descending
branches is due to friction. The actual thrust corrected for friction
may be obtained from the average of the two branches.

The actual coefficient of friction may be easily calculated. Denote
by N the total normal pressure on the external surface of the stopper.

N is approximately equal to $ph\pi\ (a + b)$ in the former notation. Then during increasing thrust we have:

$$T = N \sin \alpha + \mu N \cos \alpha.$$

and during decreasing thrust:

$$T' = N \sin \alpha - \mu N \cos \alpha.$$

We take N to be a function of the displacement only, so that for corresponding points on the increasing and decreasing branches N may be eliminated, giving:

$$\mu = \frac{T - T'}{T + T'} \frac{\sin \alpha}{\cos \alpha}.$$

Suppose, for example, that $T = 2T'$, a figure corresponding to conditions easily attained. This gives, since $\sin \alpha = 0.052$, $\mu = 0.017$. This is a coefficient of friction lower than values usually given in engineering hand books for conveniently available materials, yet even with this very low coefficient, the effective thrust on the stopper is $0.75\ T$ instead of T, and the effective external pressure at the maximum, 12,900 kg/cm^2 instead of 17,200. The extreme importance of cutting down the friction to the lowest possible value is therefore evident.

A number of experiments were made in the search for the best method of lubricating stopper and collar. In this search my shearing experiments were of great assistance,[2] as well as my former measurements of the effect of pressure on the viscosity of liquids.[3] Ordinary lubricants cease to function in the familiar ways under conditions of very high pressure. Oils and greases freeze solid, and at high pressures behave effectively like materials with high friction. The shearing experiments had shown that at high pressures the surface friction of practically every solid substance becomes so high that plastic yield takes place in the interior rather than on the surface. The obvious thing, therefore, was to find materials with minimum shearing strength. Materials with low shearing strength are tin, indium, and lead. Indium would be the best, but it is not available for obvious reasons. Lead is a little better than tin. The measurements of the shearing strength of lead indicated a strength almost proportional to the pressure in the significant range, such that the equivalent coefficient of friction is 0.016. This is a trifle lower than in the numerical example just considered. The first improvement consisted in using sheet lead as a lubricant between stopper and

collar. Assembly was made by wrapping a sheet of commercial lead foil 0.002 inches thick around the stopper before inserting the stopper in the collar. In the early work a lubricant of vaseline and graphite was used. This was fairly good; at relatively high pressures graphite loses its lubricating properties, particularly when used alone, but 17000 did not prove high enough to introduce this disturbing effect. However, the sheet lead was a distinct improvement on vaseline and graphite. Further very marked improvement was made by using an additional lubricant between both steel surfaces and sheet lead. Here the experiments on pressure coefficient of viscosity proved valuable. Water and glycerine had both been previously found to suffer comparatively small changes of viscosity with pressure; in fact the initial effect of pressure is to decrease the viscosity of water. After various trials a paste of two thirds glycerine, one third water and enough flake graphite to make it fairly stiff was found to be most effective. Under some conditions this has given coefficients of friction as small as 0.004, using the formula above for μ, which means that the external pressure on the stopper is only about 4 per cent less than the theoretical maximum. This is so near the ideal limit that it did not seem worth while to search further.

It is unfortunate that metallic sodium did not prove possible. This metal is so soft that it is very much superior to lead, but I have found that rupture has always followed contact of sodium with steel at high pressures. It is not by any means certain that some of these ruptures were not mere coincidence, but there have been so many of them that I could not help ascribing significance to them and I have therefore given up the attempt to use sodium to transmit high pressures. Perhaps it may be available under c ʼ ⁻ conditions when the pressure is not so high. Lead and glycerine and graphite has the advantage over sodium for these particular experiments that it can be used over a considerably wider temperature range.

The stopper was made of "Solar" steel. This is a silicon manganese steel made by the Carpenter Steel Co.; a typical analysis is: C 0.50; Mn 0.40; Si 1.00; Mo 0.50. Heat treatment is by quenching into water from 1550° F and then drawing back to 600°, to a Rockwell C hardness of 52 to 54. The manufacturers state that with this heat treatment the tensile strength is over 300,000 lb/in², and the elongation in 2 inches 8%. The steel therefore has a very high tensile strength combined with unusually high elongation. The elongation is so high that the inside of the stopper should stretch before breaking. The fact that this steel is water-hardening imposes the necessity for great care

in heat treatment. The change of dimensions during hardening is unusually high, and I have found a rather greater tendency for cracks to develop during hardening than in the other steels which I have used for high pressures. One useful property of the steel is that even when as hard as 52 it does not glaze the edge of the reamer, so that it is possible to stretch the stopper by a preliminary application of pressure, and then ream to final size, something that is impossible in chrome vanadium steel of as great hardness as this.

The elastic deformation of the stopper may be calculated to a rough degree of approximation by the usual formulas for a cylinder under external and internal pressure. The formula (see for example Love's Elasticity, fourth edition, p. 144) for the radial displacement in an infinitely long cylinder is:

$$u = Ar + B/r,$$

where

$$A = \frac{p_1 r_1^2 - p_0 r_0^2}{2(\lambda + \mu)\,(r_0^2 - r_1^2)}$$

$$B = \frac{(p_1 - p_0)\,r_0^2 r_1^2}{2\mu\,(r_0^2 - r_1^2)}.$$

p_1 and r_1 are internal pressure and radius, and p_0 and r_0 the corresponding external quantities. This formula neglects the longitudinal change of dimensions, which may be legitimately done for our purposes. In our case $r_0 \cong 4r_1$. Let us put $p_0 = 0.344\, p_1$, and compare the stretch at the inside surface under these conditions with that in a cylinder with infinitely thick walls subjected to the internal pressure p_1.

Case I (external and internal pressure)

$$A = \frac{p_1}{2(\lambda + \mu)} \left[\frac{1 - 5.51}{15} \right]$$

$$B = \frac{0.328\, p_1}{\mu} \left[\frac{r_1^2}{1 - 1/16} \right]$$

$$\frac{1}{p_1}\frac{u}{r}\bigg|_{r = r_1} = \frac{-4.51}{30\,(\lambda + \mu)} + \frac{.350}{\mu}.$$

Case II (infinite cylinder under internal pressure only)

$$A = 0, \quad B = \frac{p_1 r_1^2}{2\mu}$$

$$\frac{1}{p_1}\frac{u}{r}\bigg|_{r\,=\,r_1} = \frac{1}{2\mu}.$$

Take for numerical values $\mu = 7.7 \times 10^{11}$; $\lambda = 9.4 \times 10^{11}$ (Abs. C. G. S.)

Then, Case I $\qquad \dfrac{1}{p_1}\dfrac{u}{r}\bigg|_{r\,=\,r_1} = 0.0366 \times 10^{-11}$

Case II $\qquad \dfrac{1}{p_1}\dfrac{u}{r}\bigg|_{r\,=\,r_1} = 0.063 \times 10^{-11}$

In the absence of any other criterion we may take the stretch at the inner surface as a measure of the pressure which the cylinder will stand. By applying external pressure to the finite cylinder we therefore obtain an additional factor of $63/36.6 = 1.7$ beyond that possible in an infinitely thick cylinder. This factor is in addition to that obtainable by the initial stretching, which gives a factor of the order of 2. In the previous paper it was stated that the previous limit of my high pressure experiments, before using this device of automatic application of external pressure, was 20,000 kg/cm². The factor 1.7 is obviously not enough to increase the range from 20,000 to 50,000. The new increase of range depends on other factors also. It must be remembered in the first place that 20,000 did not represent the absolute upper limit by any means. By proper preliminary stretching I had already reached pressures above 40,000 in solar steel cylinders 2 inches in diameter. The benefit of this stretching gradually wore away, however. Furthermore, the former apparatus for 20,000 was 4.5 inches in diameter,[4] so that a good deal of time was involved in getting a single cylinder ready for use. These cylinders always ruptured after a number of excursions to 20,000, with possible loss of the enclosed elaborate measuring apparatus. The new apparatus, however, is very much smaller; the stoppers being only one inch in diameter can be made in a short time. The preliminary stretching can be done rapidly, and they can be got into final use a short time after the preliminary stretching. When rupture occurs there is no enclosed elaborate instrument to lose. All these factors are therefore favorable, and the new apparatus can be pushed much closer to the limit than before. The number of excursions possible to 50,000 varies a good deal; there have been a number of instances of 20 or 25 excursions. The limit may be set either by too great stretch of the interior or by fracture. Since the stoppers are so easy to make I have in my later work adopted the arbitrary rule of discarding the stopper after 12 excursions to 50,000.

As already intimated it should be possible to considerably improve on the factor 1.7 by the use of a collar of Solar steel instead of chrome vanadium, permitting the use of smaller angles of the cone and therefore a greater ratio of external to internal pressure.   In fact I am now doing this with a very much larger and more elaborate apparatus with which I have reached 30,000 in a true liquid, pressure being
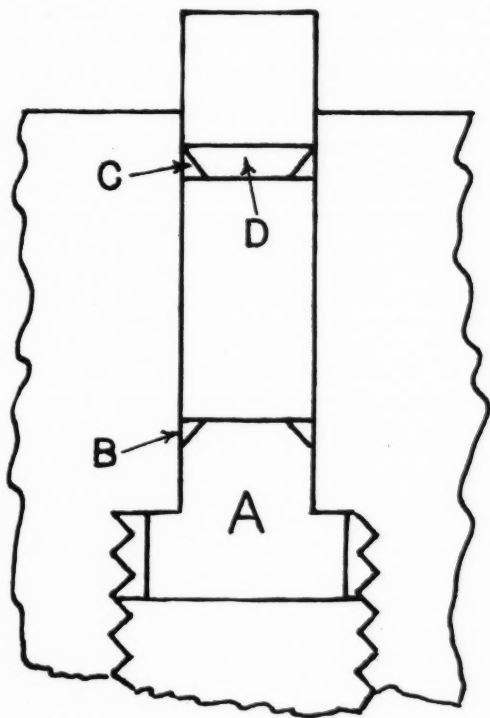

FIGURE 4.   Detail of packing.

measured with a manganin gauge through insulated leads as in my work at lower pressures.

The screw plug with which the stopper is closed at the lower end is a source of weakness.   The dimensions are such as to give an adequate

factor of safety according to ordinary methods of computation, but these high stresses cannot be handled according to ordinary rules. It appears as if the thrust cannot be distributed uniformly to all the threads along the length of the screw without a disproportionally greater displacement at the upper end. This has the effect of exceeding the elastic limit in shear of the few threads at the upper end. When pressure has been applied and released a number of times the deterioration of the thread, due to exceeding its elastic limit, gets propagated along the screw until eventually so many threads are affected that all the threads fail by shearing, and the plug is expelled with great violence. A number of very puzzling ruptures of this sort were encountered until the rule was adopted of using each screw plug for only a dozen excursions to the maximum, and since then there have been no failures of this sort. A converse sort of failure may take place if the stopper has been used a great many times with new screw plugs; the upper threads in the stopper give way, probably with the starting of fissures at the bottom of the threads; these fissures propagate themselves, and the whole bottom of the stopper gets torn off. The remedy for both sorts of rupture is to use neither stopper nor plug for more than 12 excursions to the maximum.

The screw plug is made of Cr-Va steel, heat treated by quenching into oil from 1700° F and drawing to 800° F. The central hole in the stopper is closed as shown in Figure 4 on an enlarged scale. The plug A is made of a chrome steel suitable for ball bearings (sold under the name of "Teton" by the Ludlum Steel Co.) and is left glass hard, about 65 on the Rockwell C scale. The retaining ring, B, is made of Cr-Va steel, heat treated to give a Rockwell C hardness of about 35. The closure at the upper end, which must be capable of moving as the piston advances, is made of a conical ring, C, similar to B, pushed by a bevelled disc of Teton steel, D. The angle on ring and bevel are made slightly different, so that the ring initially bears on the bevel only at its outer periphery.

The piston is a very important part of the apparatus; no steel that I have found will stand a compressive stress of 50,000 kg/cm² without continuous slow flow even if it does not immediately fracture. Carboloy proved the solution. I am greatly indebted to Dr. Zay Jeffries of the Carboloy Co. of America for supplying me with this material. There are a number of different grades of carboloy. Of all those which I tried, that marketed by the Carboloy Co. under the designation of No. 905 proved the strongest. The pistons are between 0.250 and 0.315 inches long, and have mostly been used in two diameters, 0.250 and 0.265 inches. The initial internal diameter of the stopper before

stretching is 0.250 inches. The initial stretching is usually combined with measurements on some substance, since the stretch is small and does not vitiate explorations for polymorphic transitions; for this the 0.250 piston is used. The stopper is then reamed to 0.265, and measurements made with the 0.265 piston up to the arbitrarily imposed life of the stopper. In the early work the life of the piston was seldom more than six excursions to 50,000; failure took place by chipping around the upper edge. The support afforded by the interior of the stopper at the lower edge was apparently sufficient to prevent fracture at this place. The piston was pushed at the upper end by a glass hard block of Teton steel ground flat. Taking advantage of the suggestion offered by the fact that the lower edge of the piston does not fracture, in my recent work the upper edge has been reinforced by a ring of heat treated chrome vanadium steel, 0.0625 inches thick, made a force fit for the piston. This is effective in preventing chipping at the upper edge, and the life of the piston is now much longer.

The steel plate which pushes the carboloy piston is of course not as hard as the carboloy, and the elastic limit of the steel is locally exceeded where it is in contact with the carboloy. However the steel is effectively supported by the surrounding parts, and furthermore after several applications of pressure receives an appreciable amount of work hardening (it was a surprise to me that glass hard steel can be work hardened), so that after one or two grindings of the steel surface it need receive no further attention, but apparently is good for unlimited service. Toward the end of the measurements recorded in the following the steel plate has been replaced by an insert of carboloy, 0.50 inches in diameter, ground flat. This is an improvement on the steel; it takes no permanent impression and the upper edge of the piston does not chip.

The stopper was filled with the substance on which measurements were to be made, either completely, or else almost always with the substance placed in some sort of a container. It is an obvious restriction that the substance in contact with the closure ring must be solid. The disadvantage of a solid of course is that it does not transmit a truly hydrostatic pressure. Friction of the solid on the walls of the stopper makes the pressure in the lower part of the stopper less than in the part directly below the moving piston. The error introduced by friction in this way can be roughly computed. Assuming as a crude approximation that the pressure is constant across a section, we have for the equation of equilibrium during increasing pressure

$$\pi r^2 P = (P + dP)\,\pi r^2 + \mu P\,2\,\pi r dx,$$

where μ is the coefficient of friction and x is distance along the axis. This gives

$$\frac{dP}{P} = -\frac{2\mu}{r}\,dx$$

and, on integration: $\log P = -\dfrac{2\mu}{r}x + C.$

Or, putting P_0 for the value of P at $x = 0$

$$P = P_0 e^{-2\mu x/r}$$

At the bottom of the cavity $x/r = 5$, whence

$$P = P_0 e^{-10\mu}.$$

This equation holds in the pressure domain in which surface slip occurs between the walls of the stopper and the material filling it. When pressure rises so high that the shearing strength of the material filling the stopper is reached, the coefficient of friction must be replaced by a corresponding expression involving the shearing strength.   Independent measurements of the shearing strength under pressure of many of the compounds investigated here show that the shearing strength is approximately proportional to pressure, so that the substance behaves in the high pressure range as if it had a smaller coefficient of friction than initially, but otherwise in the same way. The shearing measurements have shown that an equivalent coefficient of friction in the domain of plastic flow of 0.1 is not uncommon, so that for such substances the pressure in the bottom end of the stopper would be about one third (e^{-1}) of that exerted by the piston on the upper end.   It appears then that the effectiveness of the support afforded by friction may in many cases be prohibitively great, and it is obvious that no satisfactory measurements can be made with such substances completely filling the stopper. Lead, however, has a much lower shearing strength, and therefore a much lower equivalent coefficient of friction.   The device was therefore adopted of enclosing most of the materials in a sheath of lead.   The effective coefficient of friction is now that of the lead, which we have already seen to be 0.016.   The factor by which the pressure at the bottom is less than at the top is now $e^{-0.16} = 0.85$.   The error is larger than desirable, but not intolerable, the mean pressure in the stopper being 7 per cent less than the maximum.   In the following experiments this error is very materially further reduced as far as those phenomena are concerned which are of special interest here.   During the progress of a transition,

the substance is effectively capable of supporting no stress difference, so that at this particular point the correction for friction does not apply, and the values of equilibrium pressure and of change of volume at this point are not affected.

The method for detecting a transition and for measuring its parameters was the same as in my previous work, namely the displacement of the piston is determined as a function of pressure at constant temperature. The transition is shown by a discontinuity in the curve. The pressure of the discontinuity is now determined at different temperatures, giving the transition curve. From the magnitude of the discontinuity the change of volume may be calculated. From these data the latent heat may also be computed by Clapeyron's equation.

In determining the change of volume corrections have to be applied for the change of cross section of the stopper under pressure. This correction can be computed only roughly because in the first place the boundary conditions are not well defined, and in the second place the mathematical problem in the theory of elasticity is very complicated if one takes exact account of the fact that we are here concerned with a short cylinder in which considerable support is afforded by the ends, which are not subject to internal pressure. The solution for an infinite cylinder already used on page 51 was made the basis of the correction. The distortion produced by the external pressure, which altogether is only a small part of the total effect, was diminished by 10 per cent to allow for friction in the collar. The total distortion then calculated to arise from both external and internal pressure in an indefinitely long cylinder was arbitrarily diminished by 25 per cent, this being my guess as to the magnitude of the effective support by the ends. There results a correction factor of 1.0087 on the cross section per 10,000 kg/cm² internal pressure when the diameter of the stopper is 0.250 inches, and 1.0085 when the diameter is 0.265. These two corrections are so close that a single correction, 1.0086 per 10000 was used for both diameters. This is the correction to be used in computing Δv from the displacement of the piston. The pressure calculated from the total thrust on the piston must also be corrected for expansion of the cross section. This correction was taken as one half that just given, namely 1.0043, the reason for the factor one half being that the cross section at the ends of the region exposed to internal pressure cannot be expanded as much as the average, the shape of the internal cavity under pressure being somewhat like that of a barrel.

The total thrust on the piston was calculated from the areas and the pressure on the piston of the hydraulic press. This press was of exactly the same construction as one described in a preceding paper on shearing, and the pressure on the piston of the press was also measured with an absolute piston gauge, as there described. Friction
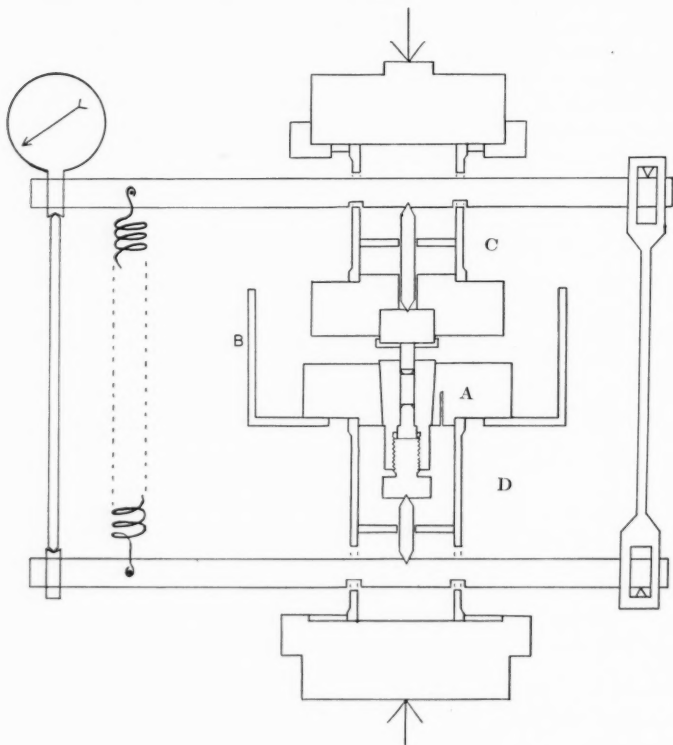

FIGURE 5. General assembly. The arrows top and bottom indicate where pressure is applied by the hydraulic press.

in the press itself was only one or two percent, as established by direct experiment. In addition to friction in the press, no doubt a very appreciable friction was offered by the conical closure immediately under the carboloy piston. All pressures recorded in the following,

unless otherwise mentioned, are means with increasing and decreasing pressure, so that frictional errors should be approximately eliminated.

In measuring the displacement of the piston during a transition a complication is introduced by the fact that the stopper in which the transition is running is itself being displaced into the supporting collar as pressure increases, so that the desired result cannot be obtained merely by measuring the displacement of the hydraulic press, as was possible in my former work. The method by which the displacement of the carboloy piston was obtained is shown in Figure 5, which gives the assembly. This diagram describes sufficiently well the arrangement of the levers by which the displacement of the carboloy piston into the stopper was measured. The levers rest against various supports, not shown, to impart the necessary stability. The motion at the end of the levers was measured with an Ames dial gauge, as shown. The magnification of the lever system was directly determined by replacing the whole central combination, stopper, carboloy piston etc. by a micrometer and determining the motion of the Ames gauge for a known motion of the micrometer. The magnification was 2.61. The Ames gauge is directly graduated to 0.001 inch, and the divisions are large enough to permit an easy estimation of tenths. A displacement of the carboloy piston of 0.00004 inches was therefore detectable. Surprisingly consistent readings were obtained; the curves of piston displacement against pressure were often smooth to about the limit of sensitiveness of the readings; the total displacement for 50,000 kg/cm² was usually between 0.1 and 0.2 inches.

In addition to the displacement of the carboloy piston, the displacement of the piston of the hydraulic press was always read as a matter of routine. This was determined from a second Ames gauge reading to 0.0001 inch by estimation, attached to the press. These readings occasionally proved useful in distinguishing between a transition and a leak (which seldom occurred), and always by taking the difference of the displacements of the two pistons provided a method of finding the displacement of the stopper into its collar, and from this permitted a determination of the friction between stopper and collar.

Temperature could be varied by means of the oil bath indicated at B in Figure 5. This bath was contained in a small sheet iron can, accurately machined and made a forced leak-proof fit for the outer part of the collar. In Figure 5 an earlier arrangement, not so good, is shown, in which the bath is soldered to the collar. Equality of temperature throughout the bath was maintained with four turbine stirrers, of about 0.5 inch diameter, driven at a high speed. Heating

was by resistance coils, spaced uniformly in the annular space outside the collar. There was no thermostatic control, but temperature was maintained constant to better than a degree by manual control, when necessary, of external resistances in the heating circuit. Temperature was determined from a copper-constantan thermo-couple inserted in the small hole A drilled in the collar. The temperature was read from the double deflections of a short period galvanometer. The couple was calibrated up to 200° against a mercury thermometer.

Pressure was transmitted to the carboloy piston by means of the steel sleeves C and D. These were made of heat treated Solar steel, of as small a cross section as was compatible with safely transmitting the compressive force. The purpose of these steel sleeves is to prevent as far as possible heat leak from the temperature bath, and to permit as uniform a temperature as possible in the specimen inside the stopper. The sleeves were accurately made, ground true after heat treatment. It is obvious that a high degree of precision is necessary in the machine work in order to prevent any side thrust on the carboloy piston, which is brittle under any force except a uniform compression.

The temperature was never pushed above 200° at 50,000 kg/cm²; at this temperature the steel becomes perceptibly softer and also the carboloy piston is weaker. Some measurements were carried down to − 80°, the oil in the bath being replaced for this purpose by a mixture of solid CO_2 and alcohol. Most transitions are too sluggish at this temperature to make measurements practical, however, and the lowest temperature of most of the measurements was room temperature.

Rupture of one sort or another is not an infrequent occurrence. The subsequent splashing of hot oil would have serious consequences, so that the entire apparatus was surrounded with a box of tinned sheet iron, with appropriate slits for the magnifying levers, the belt driving the stirrers, etc.

The routine steps of a transition exploration and measurements were as follows. The apparatus was first filled. Lead sleeves were provided to hold the material, the wall thickness of the sleeve being about 0.8 mm. The material, usually initially in a powdered condition, was placed in the sleeve in the form of little pellets which were previously compressed in a mold of alloy steel in an arbor press to a pressure between 15,000 and 20,000 kg/cm². The principal difficulty with these pellets was in removing them from the mold after formation. If the material has a high coefficient of friction or a high shearing strength it is likely to split up into a great many discs on pushing

out of the mold. For such substances the remedy is to grease the walls of the mold with a small quantity of graphite and vaseline, too small in amount to introduce appreciable error into the measurements. Sometimes even this was not successful; in such cases it was necessary to compress the powder directly into the lead sheath, which was then supported on the outside with another mold. This procedure was adopted only when absolutely necessary, it being difficult because of squeezing out of lead. When the lead sheath had been filled it was coated on the outside with a piece of copper foil 0.001 inch thick. The function of the copper was to keep the lead from direct contact with the steel. A number of unexplained ruptures had raised the suspicion that at these high pressures lead is forced into the steel, attacking it in the same way as mercury is known to do at lower pressures.[5] This precaution has apparently been effective. The lead sleeve with its copper coating was now placed in the stopper and consolidated again in the arbor press to a pressure of perhaps 20,000 kg/cm^2. Since the carboloy piston is limited in stroke it is necessary to fill the stopper so completely that the piston enters by an amount only just sufficient to keep it centered during assembly. Volume could be built up when necessary by adding bits of lead or thin stamped discs of copper above the sleeve and its contents.

In assembling the apparatus an auxiliary device or two is demanded, but it is not necessary to describe these in detail. The first run was then made at room temperature. A seasoning run was first made. At first this seasoning application of pressure was pushed only to 20,000, but it was found that on the next application of pressure irregularity of some sort always appeared in the neighborhood of 20,000, so that lately I have adopted the practice of seasoning over the entire range of 50,000. The steps in this seasoning application are 4000, and readings are made both with increasing and decreasing pressure. The zero is always displaced by a comparatively large amount after this seasoning application. If the seasoning run displays features of interest, a more careful application of pressure is then made, this time usually in steps of 2000 and at two minute intervals, although sometimes 1000 steps were used. There is always some creep after an increase of pressure, due either to slow yielding against friction or to after effects in the steel, so that it is necessary to adhere to a careful time schedule to obtain smooth readings. A two minute schedule was usually used; pressure was increased every two minutes by adding the proper weight to the dead weight piston gauge and manipulating the hand pump. One minute after increase of pressure both displacement gauges were read, and then again when

two minutes had elapsed. Pressure was then at once increased by another 2000. The dimensions of the apparatus are so small that two minutes is entirely adequate for dissipation of the heat of compression. The pressure increments in the seasoning runs were made at one minute intervals and only the one displacement reading made, at the end of the minute. In plotting the results, both the one and two minute displacements were shown. A transition is shown ideally by a discontinuity in the curve of displacement against pressure, but most transitions are sluggish, particularly at room temperature, and the corners of the discontinuity are often so much rounded, or the discontinuity itself may be so small in amount, that it is difficult to be sure of it. In such instances the creep in the readings between one and two minutes may afford welcome assistance, the creep being larger during a transition. If, after plotting the results there was reason to suspect a transition, measurements were then repeated more carefully in the neighborhood of the transition to determine its parameters more exactly. If the discontinuity was large enough, the most important datum was the equilibrium pressure, approached both from above and below. For example with increasing pressure a displacement was made corresponding to the half complete transition, the piston gauge was clamped, and pressure was allowed to spontaneously fall to its final value, determined by plotting the pressure reading on the Bourdon gauge of the hydraulic press against time. When a steady value was reached, the piston gauge was unclamped, pressure was increased, and enough readings made in the domain of the high pressure phase to enable the discontinuity in the displacement to be determined. Pressure was then decreased and the corresponding readings made. The pressure of the transition was taken as the mean of the pressures reached automatically from above and below. In many cases, however, the volume change was so small, and the amount of excess pressure necessary to start the transition so great that it was not possible to make readings of pressure on the two phase system. In such cases the transition pressure has to be taken as the mean of the pressures at which the transition spontaneously starts with increasing and decreasing pressure respectively. This value is, of course, not as accurate as the other, being obviously in error if the excess pressure required to start the transition is not symmetrical on both sides of the transition.

After the run at room temperature the oil bath was put in operation. If no transition had been found at room temperature the temperature was now set at 150° C, and a similar exploration made up to 50,000 and down. If no transition was found here either, then the substance

was set aside. If a transition had been found at room temperature, then of course measurements were made at a sufficient number of other higher temperatures to establish the phase diagram.

It is difficult to set any general estimate on the magnitude of the transitions which could be detected with this apparatus. Sometimes, when the substance has high friction, the results are much more irregular than in other cases. Some estimate of the sensitiveness can be obtained in the following from the consistency of the values for Δv.

In addition to measurements with the "stopper" apparatus, with which the volume changes are determined, all these substances were also examined with the shearing apparatus described in a previous paper.[6] Many of these shearing results are described in the following since they are pertinent in giving information about some of the properties of the new phases. Precise agreement must not be expected between the transition pressures found in the shearing and the volume apparatus, since shearing stress has a specific effect in displacing the pressure of a transition.

The presentation of detailed data now follows.

Detailed Data

Cu_2I_2. This was "c.p." stock from Eimer and Amend. The shearing curve exhibited a very pronounced maximum followed by a deep minimum, leading to the expectation of a transition.

With the volume apparatus a single transition was found with volume change large enough to permit setting on equilibrium with both phases present. This is one of the rather rare substances for which good readings could be made at solid CO_2 temperature. It is also unusual in that the width of the region of indifference becomes larger again at higher temperatures after having passed through a minimum near room temperature. The experimental points are shown in Figures 6 and 7, and the transition parameters in Table I.

TABLE I

Transition Parameters of Cu_2I_2

Pressure kg/cm²	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
16,400	−100	−.0595	.00705	20.5	.48
15,560	−50	−.0595	.00698	26.1	.61
14,720	0	−.0595	.00675	31.0	.74
13,880	50	−.0595	.00630	34.2	.80
13,040	100	−.0595	.00568	35.6	.83
12,200	150	−.0595	.00480	34.1	.80

AgCl. The material was "c.p." stock, obtained from Eimer and Amend. In the shearing apparatus indications of a transition had been found in the neighborhood of 13,000 kg/cm². Measurements were made in the volume apparatus only at room temperature and 150°, and only with increasing pressure. The change of volume is
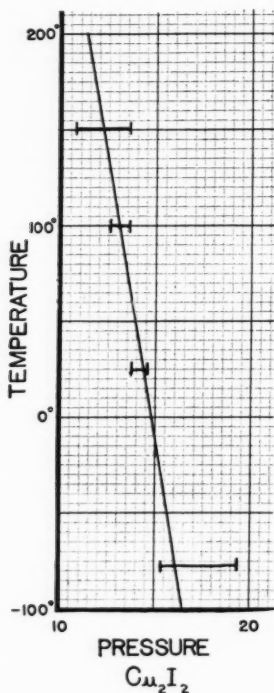

FIGURE 6. The transition line of Cu₂I₂; pressure in thousands of kg/cm² against Centigrade temperature.

small. At room temperature the transition is smeared out through two pressure steps, that is, through 4,000 kg/cm², but at 150° it ran completely on passing from one step to the next. The volume change at both temperatures was essentially the same, 0.00010 cm³/gm. At 29° a rough value for the transition pressure is 13,000

kg/cm^2, and at 150° 25,000. The latent heat demanded by these data is about 0.08 gm. cal/gm.

There was no perceptible change of slope of the displacement curve at the transition; this means that the two modifications have no large difference of compressibility.

AgBr. The material was "c.p." stock from Eimer and Amend. The shearing measurements showed no sharp break in direction, but a region of abnormal upward curvature, beginning at about 25,000
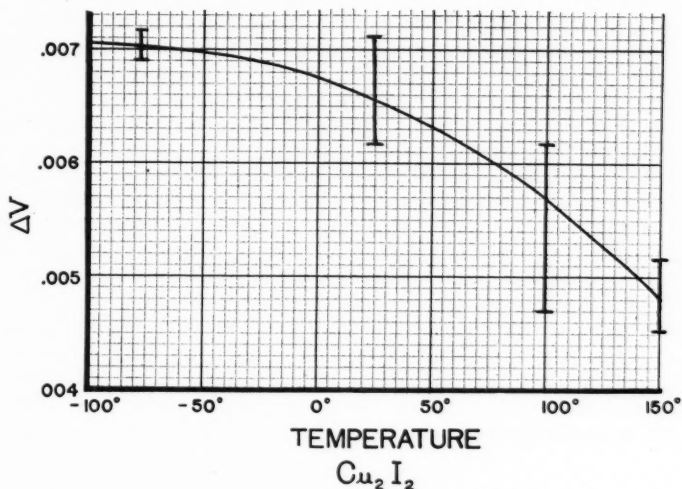

FIGURE 7.   The volume change of the transition of Cu_2I_2 in cm^3/gm plotted against Centigrade temperature.

kg/cm^2, and suggesting a transition. In the volume apparatus runs were made at room temperature, 100° and 146°. As in the case of AgCl the volume change is small, and it is difficult to disentangle the transition from other irregularities. The best values for the transition pressure were 13,000 kg/cm^2 at 20°, 18,800 at 100°, and 28,500 at 146°. The change of volume is independent of temperature within the limits of error and is 0.00015 cm^3/gm. The general character of the transition is much the same as for AgCl. Since AgCl and AgBr both have the same type of crystal structure (NaCl cubic type) the similarity of the results for both lends probability to the correctness of either.

The latent heat demanded by the above data is about 0.14 gm cal/gm at a mean temperature.

It is interesting that these two substances of NaCl type structure have transitions with such very small change of volume. The change from NaCl to CsCl type, which is produced by pressure in the ammonium, potassium, and rubidium halides, is accompanied by a large change of volume, so that a similar transition might have been expected here. Perhaps this transition is similar to the curious transition of RbCl with small volume change at low pressures.[7]

Ag₂S. The material was from Kahlbaum. The shearing curve was of the conventional type, concave toward the pressure axis over the entire range, and with a rather definite knee. There was some slight irregularity beyond the knee that might have been taken to indicate the possibility of a transition, but the effects were very small and the transition most doubtful.

Runs were made in the volume apparatus at four temperatures from room temperature up to 188°. There is a transition with small change of volume, too small to permit settings to be made on the two phase system. At room temperature the transition was not found at all, doubtless because of too great sluggishness. At the higher temperatures the volume change during decrease of pressure was more abrupt than with increasing pressure, giving better values for change of volume with decreasing pressure. The values for change of volume were in any event uncertain enough, and justify only one significant figure; the accuracy does not justify the attempt to deduce what the variation of change of volume is along the transition line.

TABLE II

TRANSITION PARAMETERS OF Ag₂S

Pressure kg/cm²	Temperature °C.	$\frac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	Latent Heat gm cal/gm
15,300	100	.0135			
19,000	150	.0135	.0005	16.	0.4
22,700	200	.0135			

The experimental points for transition pressure as a function of temperature are shown in Figure 8. It is not worth while showing a diagram for the change of volume. The transition parameters are given in Table II, assuming a constant and very rough value for volume change.

Ag₂S is known to have a polymorphic transition at atmospheric pressure at 180°. This is so near the maximum temperature of these

measurements that one could not expect to find the transition, and it is obvious that the transition studied here is not the same and is new.

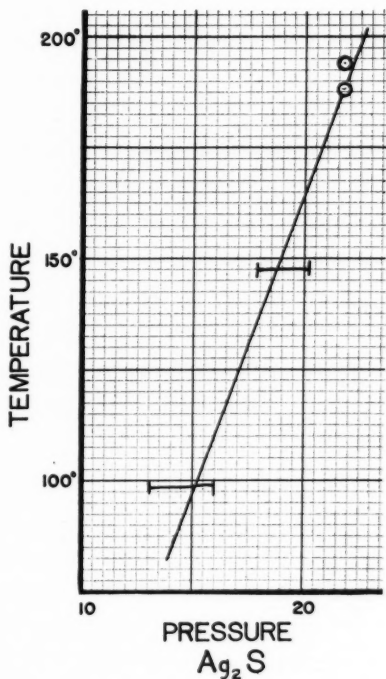$ZnBr_2$.   This was "c.p." stock from Eimer and Amend.   It is very

FIGURE 8.   The transition line of Ag_2S; Centigrade temperature against pressure in thousands of kg/cm².

hygroscopic; it was dried by heating in vacuum to 130° and immediately placed in the pressure vessel.

The shearing curve had shown a very marked maximum at about 26,000 kg/cm² at room temperature of a character that almost certainly meant a transition or else decomposition to the metal.

In the volume apparatus a transition was found at once in the expected place with a comparatively large volume change.   Measure-

ments were made at five temperatures from room temperature up to
150°. There was some irregularity in the high pressure readings
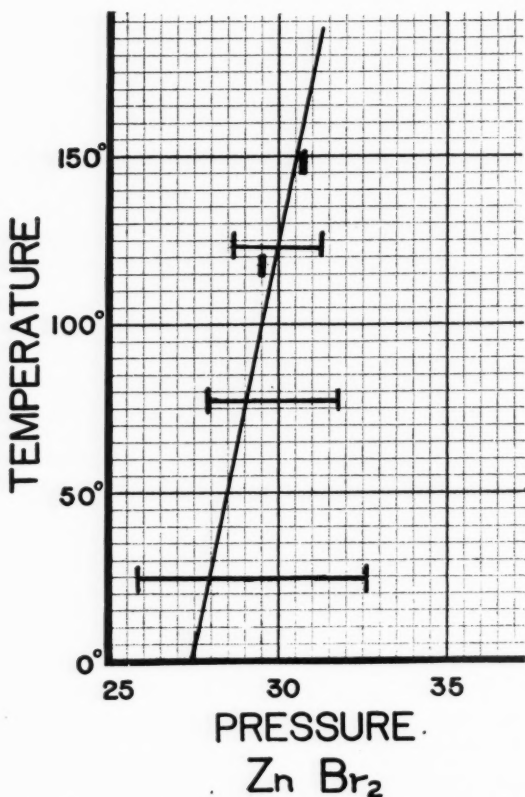which raised the suspicion that there might be two transitions close

FIGURE 9.   The transition line of ZnBr$_2$; Centigrade temperature against
pressure in thousands of kg/cm^2.

together. I was not able to obtain any positive evidence that this is
the case, but I believe that the possibility is not entirely excluded.
At the low pressure end at the higher temperatures there were also

marked irregularities. The interpretation finally adopted for these irregularities is that there is a transition at atmospheric pressure in the neighborhood of 125°, which at 150° runs at something of the order of 1500 kg/cm² and with a volume change of the order of 0.01 cm³/gm. This apparatus is not adapted to good measurements in this range, and I let the matter go without trying for improved
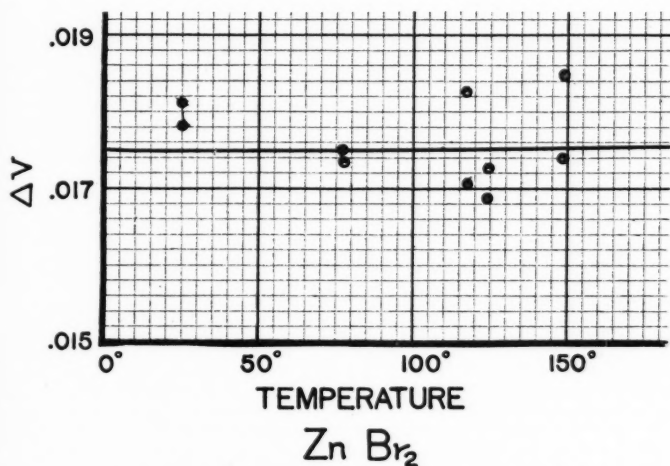

FIGURE 10. The volume change of the transition of ZnBr₂ in cm³/gm plotted against Centigrade temperature.

values in another apparatus. No previous record seems to have been made of a transition at atmospheric pressure according to Mellor.

The experimental results for the high pressure transition are shown in Figures 9 and 10, and the transition parameters are collected in Table III.

TABLE III

TRANSITION PARAMETERS OF ZnBr₂

Pressure kg/cm²	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat	
				kg cm/gm	gm cal/gm
27,500	0	+.0500	.0175	96	2.24
28,500	50	+.0500	.0175	113	2.65
29,500	100	+.0500	.0175	131	3.06
30,500	150	+.0500	.0175	148	3.47

$HgCl_2$. The material was "c.p." stock from Eimer and Amend.
The shearing curve did not give any striking evidence for a transition;
there was however, a gentle inflection above the knee in the curve at
25,000 which suggested the possibility. Four different fillings of the
pressure apparatus were made. With the first filling runs were made
at room temperature to 50,000 and back, and at 150° to 45,000, where
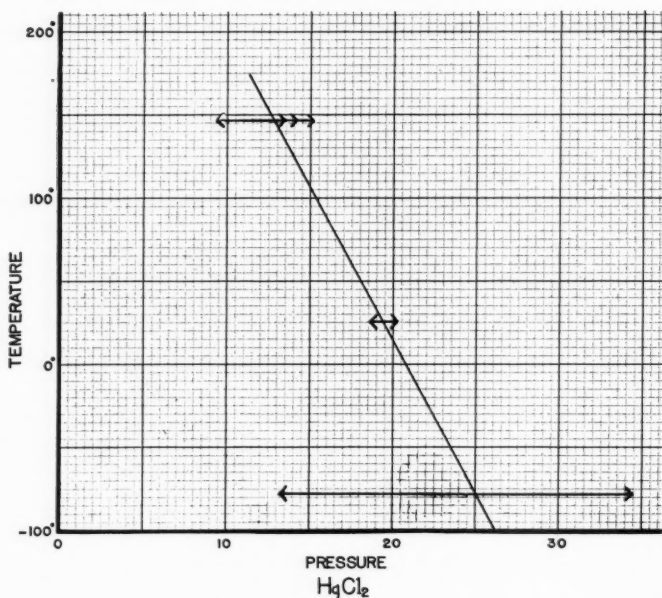there was an explosion, the stopper pulling apart at the root of the

FIGURE 11. The transition line of $HgCl_2$; Centigrade temperature against
pressure in thousands of kg/cm².

lower thread. With this run the existence of the transition was es-
tablished. Values of Δv were found at room temperature, both with
increasing and decreasing pressure, although the transition was
somewhat sluggish and therefore spread over a range; at 150° a good
sharp volume discontinuity was obtained. With the second filling
at 150° the stopper ruptured again in the same way at about 30,000,
but not until readings had been made on the transition. The third

filling gave readings on the transition at 150°, both with increasing and decreasing pressure, but there was so much creep that I thought it advisable to make a blank run with lead to determine if possible the
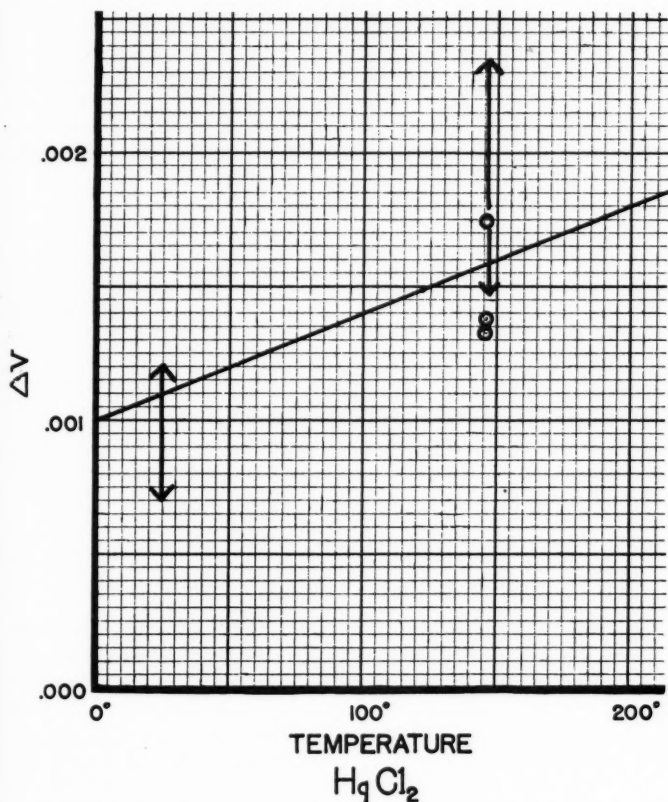

FIGURE 12. The volume change of the transition of $HgCl_2$ in cm³/gm plotted against Centigrade temperature.

cause of the creep. This blank run was again terminated by the same sort of rupture. This type of rupture was traced to the screw plug, which had been used so many times that the threads were beginning to shear off. As already explained, the remedy is to use the screw

plug for only a limited number of excursions to the maximum. A
fourth set-up and run was now carried out without rupture of the
stopper. The last run with this set-up was made at CO_2 temperature.
Here the transition could be detected, principally by increased creep,
but the transition was so sluggish, and the corners of the displace-
ment curve so rounded that good values of Δv could not be obtained.
The final run was at 150°. This gave good values for the transition
pressure and for Δv both with increasing and decreasing pressure.
At pressures beyond the transition it was found, however, on plotting
the results, that there had been mechanical interference with free
motion of the lever giving the piston displacement, so that none of
these runs have yet answered the question of whether there may not
be still another transition at 150° at pressures above the maximum
at which satisfactory readings were obtained, that is, about 45,000.

The experimental results are shown in Figures 11 and 12 and Table
IV. The transition is of the ice type. A Δv increasing with increasing
pressure is common with this type of transition.

TABLE IV

Transition Parameters of $HgCl_2$

Pressure kg/cm²	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
20,800	0	− .0183	.0010	14.9	.35
15,300	100	− .0183	.0014	28.6	.67
12,600	150	− .0183	.0016	37.0	.87

HgBr₂. The source of the material was Eimer and Amend, "c.p."
stock. The shearing measurements showed two downward breaks,
one in the vicinity of 12,000 and the other in the vicinity of 25,000.
Beyond the last break the shearing curve was very markedly concave
upward, an unusual effect. Both of these breaks are similar to the
"knee" shown by normal substances, so that the interpretation of
the curves in terms of a transition is difficult.

In the volume apparatus three new modifications were found, with
three transition lines running nearly vertically. With the regular
volume apparatus exploration was made to 50,000. In all, eight
different runs were made with this apparatus, with a single filling,
without accident. At the conclusion of the runs a small drop of free
mercury was found, indicating some decomposition. The amount of
decomposition was so small, however, that there should be no appreci-
able error in the results. The low pressure transition runs at pres-
sures so low that it could not be measured accurately enough with the

regular apparatus. Accordingly this transition was measured in a similar apparatus with piston 0.375 inches in diameter instead of 0.265. Six different runs were made with this apparatus. No decomposition to free mercury was observable, suggesting that the effect found with the other apparatus was the result of high pressure. This transition becomes rapidly sluggish at low temperatures.

The experimental results are shown in Figures 13 and 14, and the best values of the transition parameters in Table V.

TABLE V

TRANSITION PARAMETERS OF $HgBr_2$

Pressure kg/cm^2	Temperature °C.	$\dfrac{dz}{dp}$	ΔV cm^3/gm	Latent Heat	
				kg cm/gm	gm cal/gm
		I–II			
1,700	50	0.167	.00185	3.57	.084
2,000	100	0.167	.00185	4.15	.097
2,300	150	0.167	.00185	4.71	.110
2,600	200	0.167	.00185	5.26	.113
		II–III			
23,000	50	.0455	.00112	7.9	.186
24,100	100	.0455	.00102	8.4	.196
25,200	150	.0455	.00092	8.5	.200
		III–IV			
39,200	0	−.0937	.00204	5.9	.139
38,700	50	−.0937	.00219	7.5	.177
38,100	100	−.0937	.00235	9.3	.219
37,600	150	−.0937	.00250	11.3	.264

The phase diagram of $HgBr_2$ is seen to be entirely different from that of $HgCl_2$. This is to be expected from the crystal structure. According to Wyckoff, although both belong to the ortho-rhombic system, the space groups are different; $HgCl_2$ is a molecular lattice, while $HgBr_2$ is a layer lattice.

HgI_2. The material was from the stock room of the Harvard Chemical Laboratory. This substance has a known transition at atmospheric pressure at 127°, where the ordinary red modification changes to yellow. I have previously studied this transition up to 12,000 kg/cm^2.[8] It is the only transition found so far which has a maximum transition temperature, beyond 5,000 kg/cm^2 and 181° the transition line falling with increasing pressure. The transition becomes very sluggish on the falling branch, however, and I did not follow it beyond 60°. Four runs were made with the present appa-

ratus, at room temperature, 100°, and two at 146°. The known transition from red to yellow was found at all temperatures, with values for the transition pressure and change of volume which agreed with the former values within the limits of error everywhere except for the change of volume at 146°, which was now found somewhat
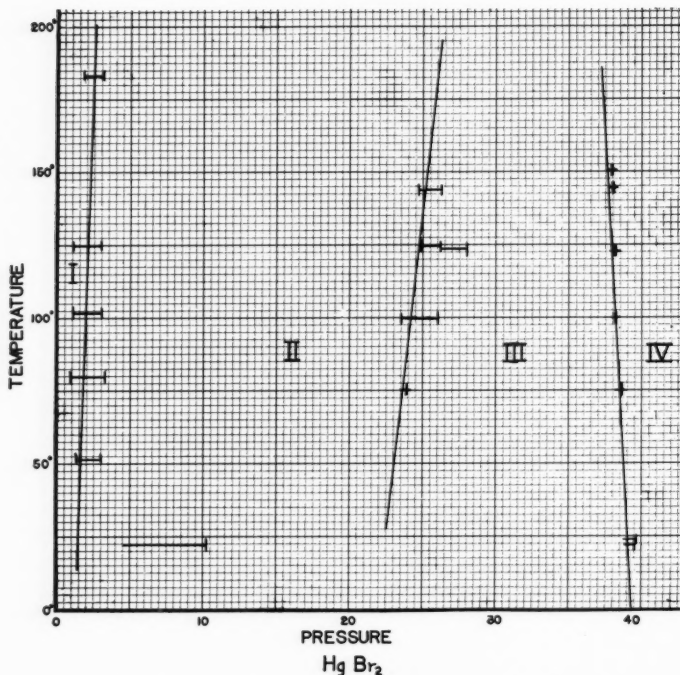

FIGURE 13. The phase diagram of HgBr₂; Centigrade temperature against pressure in thousands of kg/cm².

higher than before. At room temperature the difference of transition pressure from above and below was only 1,000 kg, and the transition was not particularly sluggish. The sluggishness of a transition may be affected by many factors; it may be that the lead sheath in which the material was enclosed accounted for the present greater liveliness of the transition.

The greatest interest of these measurements of course lies in the possible discovery of other transitions.   Both runs at 146° gave evidence for a small transition so near the upper end of the pressure range that with increasing pressure the volume change could not be
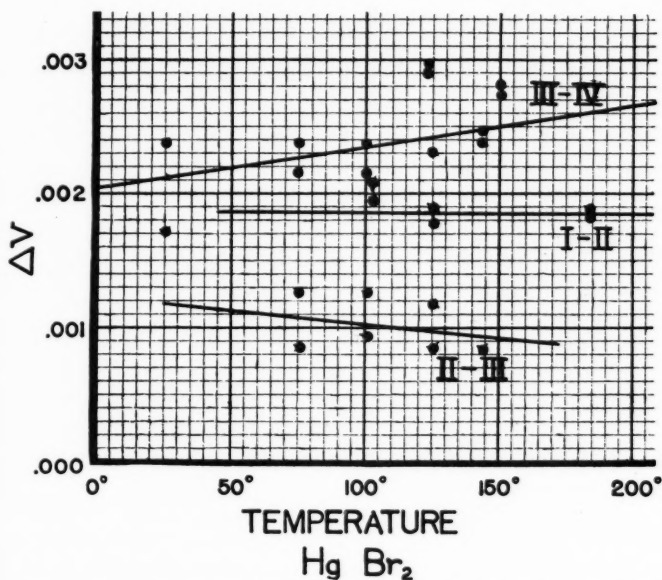

FIGURE 14.   The volume change of the transitions of $HgBr_2$ in cm³/gm against Centigrade temperature.   The apparently scattered points are to be associated with the nearest line.

disentangled from creep, which occurred with the particular stopper used for this exploration at a pressure lower than usual.   The best values for the pressure of transition at 146° are 41,300 to 43,600 kg/cm², and the volume change is of the order of 0.0004 cm³/gm. This transition was not picked up at either of the other temperatures, so the latent heat cannot be computed.

The shearing curve had three possible small breaks, the significance of which is most doubtful, but in addition there was one very well defined upward break, of the character that almost invariably means a transition, at 25,000 kg/cm².   The interpretation is doubtful; if this

is the ordinary red-yellow transition then the transition pressure is displaced by an unusual amount by the shearing stress. It is not
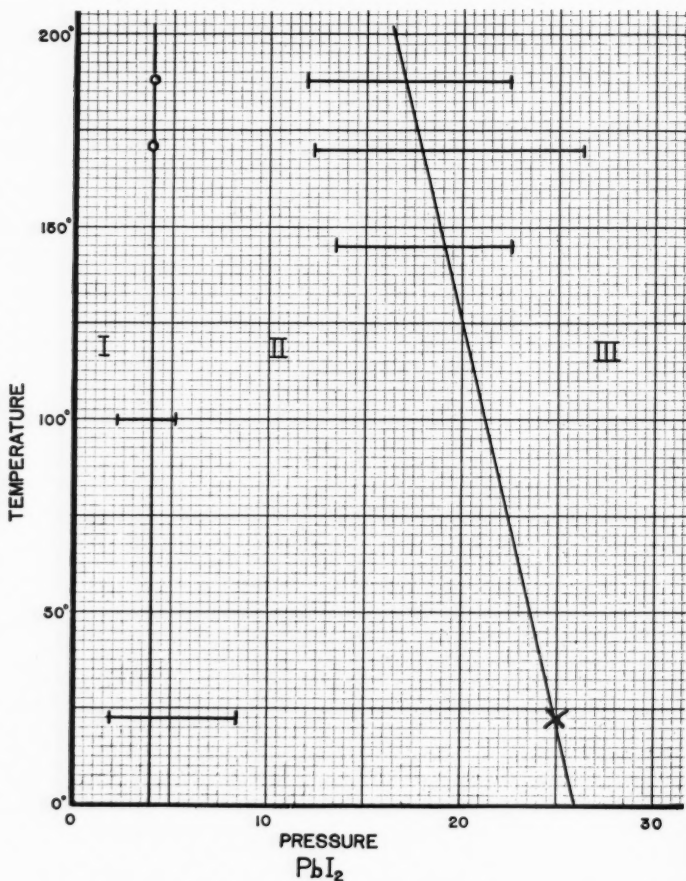

FIGURE 15. The phase diagram of PbI₂; Centigrade temperature against pressure in thousands of kg/cm².

unlikely that it is the transition found with the volume apparatus at 146°; the reason that it was not found with the volume apparatus

at room temperature must in this event be set down to too great sluggishness.

GeI₂. This material I owe to the kindness of Professor K. T. Bainbridge, who in turn obtained it from Professor Albert W. Noyes, Jr. There was a sharp downward break of an unusual character in the shearing curve near 18,000 kg/cm². In the volume apparatus the
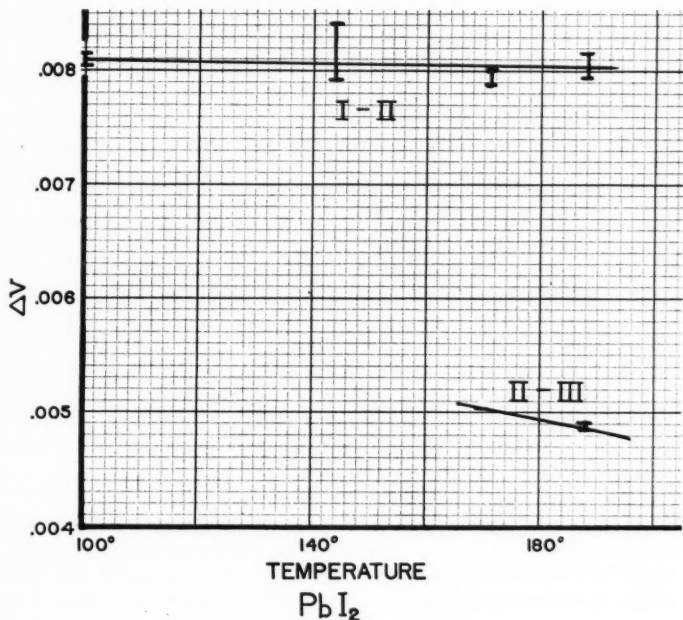

FIGURE 16. The volume change of the transitions of PbI_2 in cm³/gm against Centigrade temperature.

first run with increasing pressure gave apparently a small discontinuity in volume at about 19,000. The reverse transition with decreasing pressure could not be definitely established; there was a definite break in direction of the piston displacement curve, but this occurred at the pressure where the stopper begins to move out of the collar, and the two effects could not be disentangled. A second run at room temperature, this time at 1,000 kg pressure intervals and four minute

time intervals, gave results more irregular than those of the first run, but not inconsistent with them. At 150° a somewhat smaller volume discontinuity was found at 29,000. On the whole the probabilities favor a transition at the pressures stated, with a volume discontinuity of the order of 0.0001 cm^3/gm.

PbI_2. This was "c.p." stock from Eimer and Amend. The crystal structure is hexagonal, of the CdI_2 type. The shearing measurements showed a definite, but not striking, upward break at 26,000 kg/cm^2, suggesting a transition. In the volume apparatus seven different runs were made, with a single filling and no accident. There are two new modifications, each with a comfortably large volume change. The transition which occurs at the higher pressure runs with practical velocity only at the higher temperatures; at 144° it had become so sluggish as to be difficult, and it could not be detected at all at room temperature. This is without doubt the transition found with the shearing apparatus; we have here another example of the effectiveness of shearing distortion in overcoming internal viscosity. The other transition which runs at comparatively low pressures has so far lost its sluggishness at the three highest temperatures that the width of the band of indifference vanishes, but at 100° and especially at room temperature the band of indifference is important.

The phase diagram is shown in Figure 15, the volume change in Figure 16. It is evident that the band of indifference is so wide that any values assumed for $d\tau/dp$ must be rather hypothetical. I have therefore not ventured to give a table of the parameters of the transition.

Cr_2O_3. The material was "c.p." stock from Eimer and Amend. Ordinarily a substance with as high a melting point as this has would not have been tried, because transitions of such substances are usually impossibly sluggish in my temperature range. The shearing measurements however, had shown an unusually definite indication of a transition at room temperature in the neighborhood of 28,000 kg/cm^2, the shearing curve at this point taking a small abrupt dip and then rising abnormally at a continually accelerating pace at higher pressures.

Careful explorations were made with the volume apparatus on the two minute schedule at 150° and 175°. Apparently there is a sluggish transition beginning at both these temperatures at 26,000 kg/cm^2 with increasing pressure and running over a pressure interval of 8,000 kg/cm^2. The volume change is of the order of 0.0004 cm^3/gm. However, the evidence with regard to this transition is not as satisfactory as could be desired; there was no sign of the transition with decreasing pressure, and in the pressure range of the suspected

transition the creep was no more rapid than outside the range. Neither of these points is decisive, however, and on the whole I believe the evidence favors the transition.

KCN. This was fresh "c.p." stock from Eimer and Amend. The shearing curve gave a very definite indication of a transition, having a sharp upward break in direction. This means that the high pressure phase has a higher shearing strength than the low pressure phase. The pressure of the break was 26,000 kg/cm². With the volume apparatus eight different runs were made, with a single filling, without accident, from CO_2 temperature to 146°. The transition phenomena are rich, and three new modifications were found. The transitions mostly run rapidly, and in some cases with unusually large volume changes, so that equilibrium pressures could be read with both phases present, with the result that unusually satisfactory values were obtained. This is one of the few substances for which good values were obtained at CO_2 temperature. A transition was first picked up at this temperature, which ran so sharply that when correction was made for friction the width of the band of indifference proved to be zero. It was again found at room temperature, of course also running without appreciable band of indifference. At 75° the transition had split into two, each running without appreciable band of indifference, one of the transitions carrying most of the volume change. At 100° the expected transitions II–III and III–IV were found at high pressure, but on plotting the results it was evident that a new transition had put in its appearance at low pressures. Not enough readings were obtained to give the volume change of this new transition. Further measurements between 85° and 150° substantiated the existence of a transition at comparatively low pressures, of a quite different character from the others. This transition is sluggish, the sluggishness rapidly increasing with decreasing temperature, which is doubtless the reason that it was not found at room temperature. Furthermore, the coordinates found first at 100° do not fit at all with the other coordinates found later for the new low pressure transition; the only possible explanation is that the transition first found at 100° is of an absolutely unstable form. The relations are such that it must be the low pressure form that is unstable, so that it is to be anticipated that under proper conditions, including perhaps previous exposure to high pressure, an absolutely unstable form can be realized at atmospheric pressure.

The experimental points are shown in Figures 17 and 18, and the transition parameters are given in Table VI. The parameters for the transition I–II are very rough; the best of them is probably Δv.
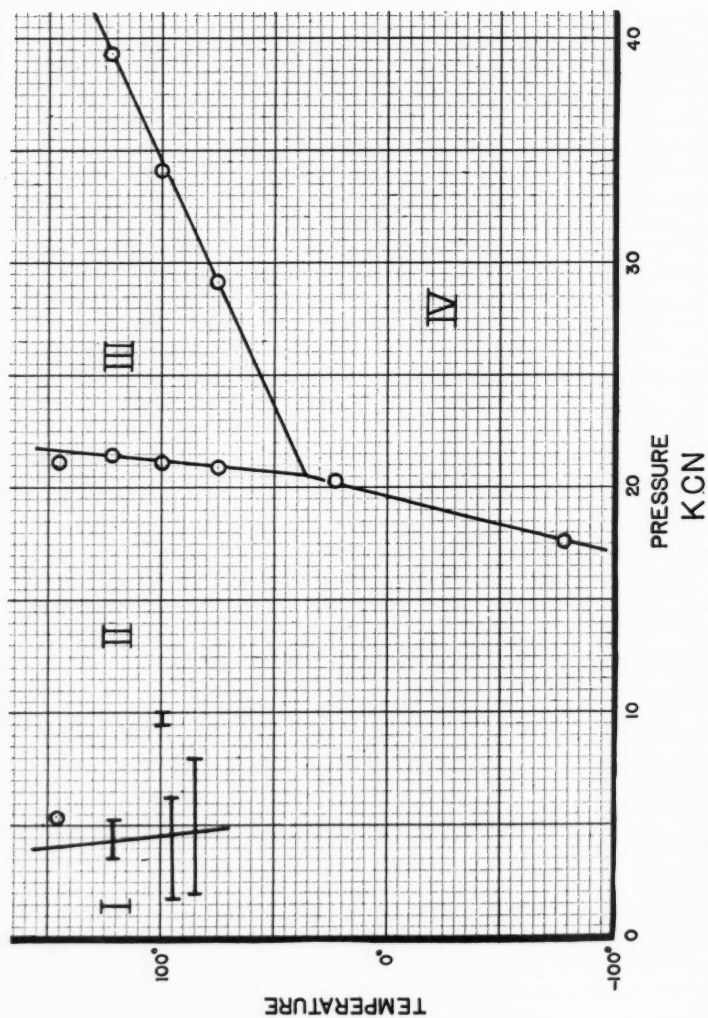
FIGURE 17.   The phase diagram of KCN; Centigrade temperature against pressure in thousands of kg/cm².

TABLE VI

Transition Parameters of KCN

Pressure kg/cm²	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
		I–II			
4,800	80	−.0875	.0150	61	1.42
4,000	150	−.0875	.0230	111	2.61
		II–III			
20,660	50	.0895	.0553	199	4.67
21,220	100	.0895	.0530	221	5.18
21,780	150	.0895	.0507	239	5.62
		II–IV			
17,700	−80	.0417	.0638	295	6.91
18,900	−30	.0417	.0620	361	8.46
20,100	+20	.0417	.0602	423	9.91
		III–IV			
23,540	50	.00461	.0034	238	5.58
32,220	90	.00461	.0025	197	4.62
40,900	130	.00461	.0016	140	3.28

Triple Point II–III–IV

Pressure kg/cm²	Temperature °C.		$\dfrac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
		II–IV	.0417	.0595	441	10.36
20,500	36°	II–III	.0895	.0558	192	4.51
		III–IV	.00461	.0037	248	5.82

KCN is cubic, NaCl structure. The fact that the phase diagram is so much more complicated than that of any of the simple ionic compounds of this structure suggests that the CN radical may not continue to function as a single unit at high pressures.

AgCN. The material was "c.p." stock from Emier and Amend. The shearing curve showed a gentle upward break at 17,000 kg/cm², suggesting a transition. Four runs were made in the volume apparatus: at CO_2 and room temperatures, 90°, and 147°, with a single filling and without accident. Although no transition was found at CO_2, one was found at the three others. The volume change was so small that it was not possible to obtain readings on the two phase system, for when the transition started it ran to completion. The high pressure phase is distinctly less compressible than the low pressure phase. This results in considerable uncertainty in the change of volume when there is as wide a region of indifference as here. The change of volume is roughly 0.0002 cm³/gm; a greater degree of accuracy is not justified

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by the results. The experimental values of transition pressure and temperature are shown in Figure 19. Sufficiently accurate values
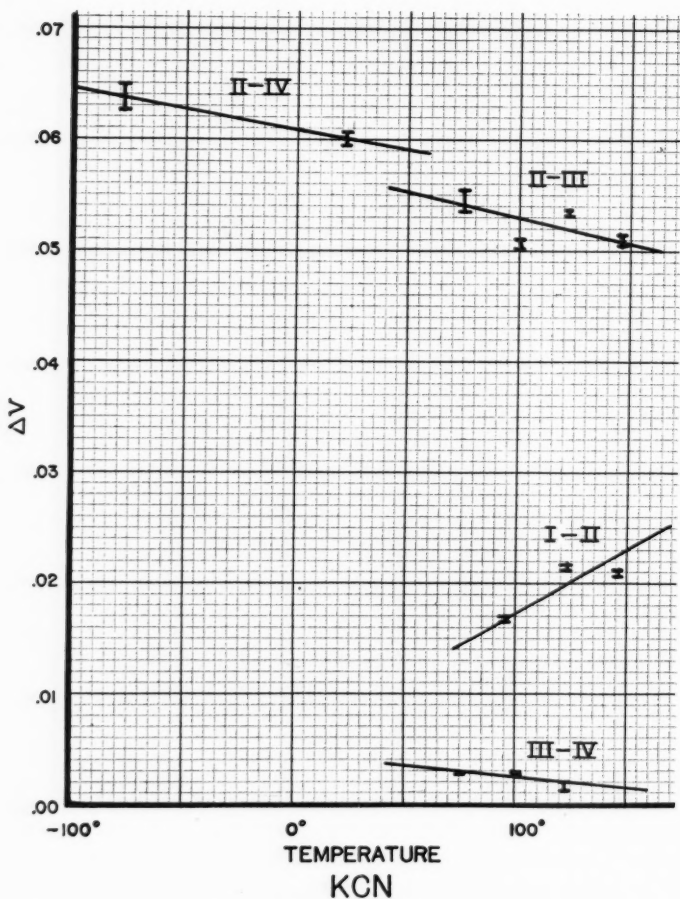

FIGURE 18. The volume change of the transitions of KCN in cm³/gm against Centigrade temperature.

of the transition parameters can be taken from the figure, so that a table is not necessary.
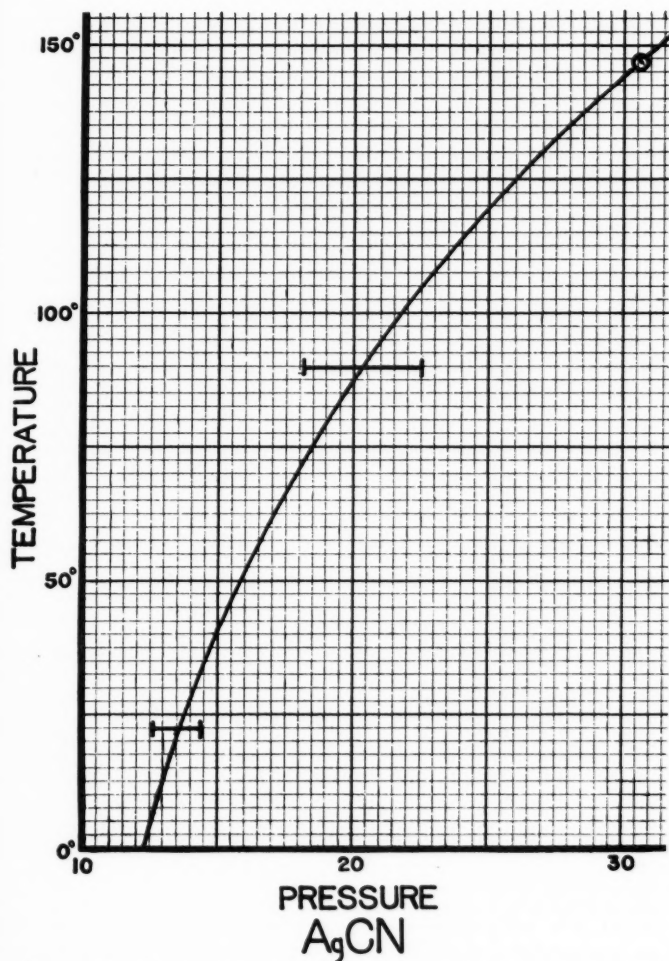
FIGURE 19.   The transition line of AgCN; Centigrade temperature against pressure in thousands of kg/cm².

AgCN is ortho-rhombic in structure, entirely unlike KCN so the great dissimilarity in phase diagrams is not surprising.

$NaNO_2$. The shearing curve suggested a transition because it takes a gentle upward bend in the neighborhood of 15,000. Five different runs were made in the volume apparatus with two set-ups, one
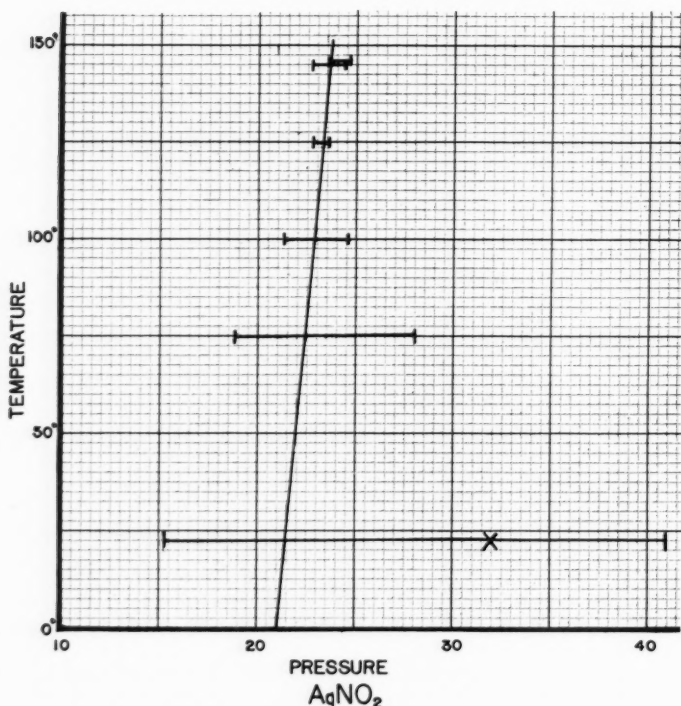

FIGURE 20. The transition line of $AgNO_2$; Centigrade temperature against pressure in thousands of kg/cm^2. The cross shows the point of discontinuity on the shearing curve.

terminated by an explosion. Explorations were made at CO_2 and room temperatures and 150°. No definite volume discontinuities could be found, but there were very sharp breaks in the direction of the curves at 150°. These breaks were obtained on both runs, were

found with increasing and decreasing pressure at approximately the same place, and could not well have been frictional effects on the outside of the stopper, as shown by a plot of the displacement of the stopper into the collar against pressure. At the other temperatures similar effects were found but less definite. It is probable that there is a transition with very small volume change, the high pressure phase being less compressible than the low pressure phase by approximately 5.0×10^{-7} (in kg/cm^2 units and assuming 2.25 for the density). The transition pressure probably rises with temperature. If the somewhat
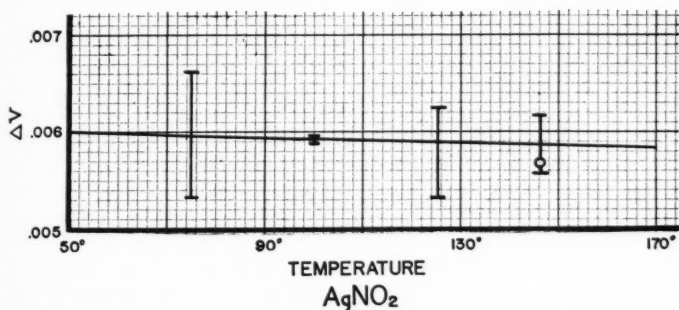

FIGURE 21. The volume change of the transition of AgNO$_2$ in cm^3/gm against Centigrade temperature.

doubtful indications at $- 80°$ are taken at their face value, the transition curve rises from 6,000 kg/cm^2 at $- 80°$ to 17,000 at 150°.

KNO$_2$ has a transition with a transition line already studied[9] of somewhat the same general character as that just suggested for NaNO$_2$, but running at pressures of the order of 5,000 kg/cm^2 lower. The volume change for KNO$_2$ is fairly large. The crystal system of NaNO$_2$ is ortho-rhombic; that of KNO$_2$ has apparently not been determined.

AgNO$_2$. The material was "c.p." stock from Eimer and Amend. The shearing curve had given unusually clear indications of a transition, there being a large and sharp upward break at 33,000 kg/cm^2, which means that the high pressure modification has the higher shearing strength. Seven different runs were made in the volume apparatus at temperatures from $- 80°$ to 150°, with a single filling and without mishap. There is a transition which rapidly becomes

sluggish at low temperatures; no trace was found of it at $-80°$, and only doubtful indications at room temperature. At $115°$ and $150°$, on the other hand, the transition ran sharply, approximately the same equilibrium pressure being approached from above and below.

The experimental results are shown in Figures 20 and 21, and the transition parameters in Table VII.

TABLE VII

TRANSITION PARAMETERS OF AgNO$_2$

Pressure kg/cm^2	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm^3/gm	Latent Heat kg cm/gm	gm cal/gm
21,000	0	.0556	.00607	29.8	.70
21,900	50	.0556	.00600	34.8	.82
22,800	100	.0556	.00593	39.7	.93
23,700	150	.0556	.00586	44.5	1.09

The high pressure modification is markedly less compressible than the low pressure form, the difference being of the order of 5×10^{-6}, assuming 2.5 for the density.

RbNO$_3$. This material was obtained from Mackay. The shearing measurements showed a smooth curve, with no suggestion of a transition.

RbNO$_3$ is known to be polymorphic at atmospheric pressure, there being three modifications and two transition points at $164°$ and $219°$. I have previously[10] studied the transition line starting at $164°$; it rises with pressure to $218.6°$ at 6,000 kg/cm^2, and with a volume change falling from 0.0069 cm^3/gm at atmospheric to 0.0043 at 6,000 kg/cm^2.

One new modification was found in the higher pressure range. The volume change is considerably less than that of the transition previously measured, and it was not possible to set exactly on equilibrium. The transition is very sluggish, with a wide region of indifference, at the lower temperatures, but at the two highest temperatures the region of indifference becomes vanishingly small. The sluggishness at the lower temperatures was so great that measurements of the change of volume were not possible there. Even at the higher temperatures the changes of volume could be determined with much less accuracy than usual.

The experimental results are shown in Figures 22 and 23, and the thermodynamic parameters are collected in Table VIII. There is considerable uncertainty in the slope of the transition line; it may well have curvature in abnormal direction. The general trend of the transition line is to rise more rapidly than the line already studied, so

that a triple point at considerably higher temperatures may be suspected.

TABLE VIII

TRANSITION PARAMETERS OF RbNO$_3$

Pressure kg/cm^2	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm^3/gm	Latent Heat kg cm/gm	gm cal/gm
16,500	0	.0211	.0017	22.0	0.54
18,900	50	.0211	.0021	32.2	0.79
21,300	100	.0211	.0025	44.2	1.08
23,700	150	.0211	.0029	58.2	1.42
26,000	200	.0211	.0033	74.1	1.82

$CsNO_3$. I am indebted for this material to Professor G. P. Baxter; it was of exceptional purity. The shearing measurements gave a smooth curve, with no hint of a transition.

This substance has a known transition at atmospheric pressure at 154°, and in my previous work the effect of pressure on the transition was studied up to 6,000 kg/cm^2 and 207°.[10] In the present work examination was made for other transitions to 50,000 kg/cm^2 at room temperature, 125°, 150°, and 175°. Nothing new was found at room temperature, but at the three higher temperatures there is fairly certain evidence of a transition with very small change of volume at pressures between 25,000 and 30,000. In addition to this new transition, the transition formerly studied was picked up at the lowest end of the pressure range at 175°, but no attempt was made to redetermine the parameters.

The experimental values for the transition pressures are shown in Figure 24. The change of volume is of the order of 0.00015 cm^3/gm, with a large degree of uncertainty. In view of the uncertainty of the results it did not seem worth while to attempt to calculate the other parameters of the transition.

$AgNO_3$. The material was old "c.p." stock from Merck. This substance has already been studied up to 12,000 kg/cm^2.[10] There is a transition at atmospheric pressure at about 160° of the ice type; the transition line runs downward, reaching 7,000 kg/cm^2 at 100°; not far beyond this the transition line experiences an abnormally large downward curvature such that at 0° C the pressure has risen to only 9,800 kg/cm^2. The curvature and various irregularities in the change of volume raised the suspicion at the time of the early work that there might be other modifications, but I was not successful in finding any.

The shearing measurements gave a curve for room temperature
with a very pronounced upward break at about 16,000, and smooth
beyond the break up to 50,000.   The break was interpreted as due to
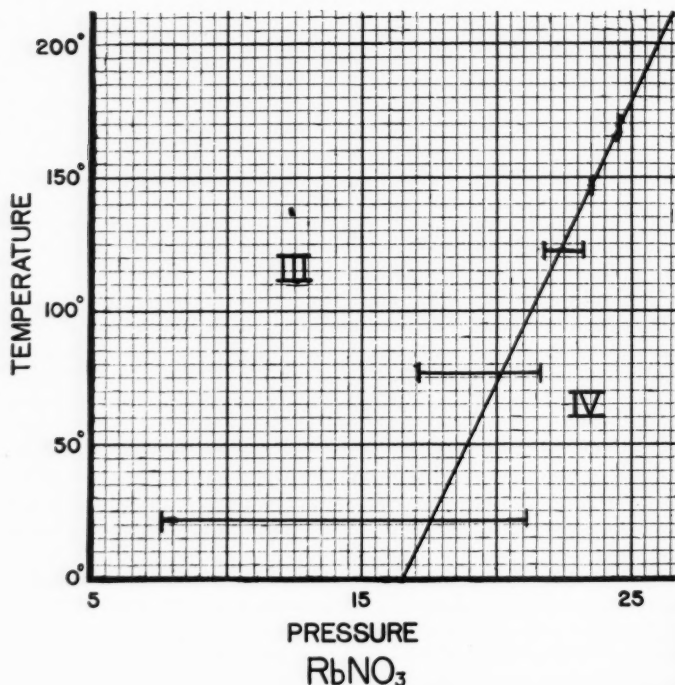the known transition.

FIGURE 22.   The high pressure transition line of $RbNO_3$; Centigrade
temperature against pressure in thousands of kg/cm^2.

The first study with the volume apparatus was made at solid CO_2
temperature, the object being to find whether the great curvature
just above 0° C continues to lower temperatures.   It was anticipated
that the transition would be difficult to locate because the majority
of transitions become impractically sluggish at this temperature, and
in particular the transition was rapidly becoming more sluggish when
last studied at 0° C.   The transition was found, but it was not par-

ticularly sluggish, so that the equilibrium pressure could be shut within fairly narrow limits. Furthermore the pressure was higher than anticipated, so that the transition line already known would have to reverse its direction in order to reach the new point, and the change of volume was also considerably larger than expected. Unfortunately the apparatus was taken down before the significance of these results was appreciated, the probable interpretation, of course, being that there must be another modification. The apparatus was
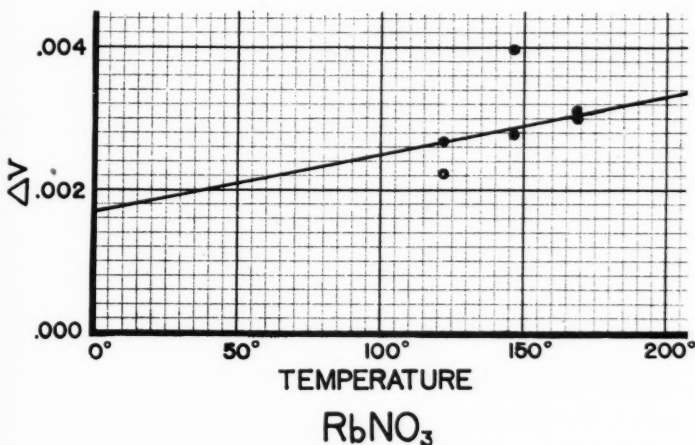

FIGURE 23. The volume change of the high pressure transition of RbNO₃ in cm³/gm against Centigrade temperature.

then set up again and measurements made at higher temperatures. There did indeed turn out to be other modifications, two at least with comfortably large volume changes, running at pressures beyond 30,000. The transition lines run fairly nearly vertically, and so close together that some care is necessary to disentangle them.

The transition III–IV with the largest volume change, about 5 per cent, occurs at pressures near 40,000. Considerable superpressure is necessary to start the transition; the result is that changes of volume for this transition could be measured only with decreasing pressure. With increasing pressure approximately 50,000 is necessary to start the transition at room temperature and at 50,000 there is appreciable creep in the apparatus. At higher temperatures it is

true the pressure of the transition becomes somewhat lower and the amount of super-pressure less, but at the same time creep occurs at lower pressures, so that the net result was that at no temperature could creep be disentangled from the legitimate volume change with increasing pressure. The volume change was large enough, however, so that there was no difficulty in establishing the pressure of the transition with increasing pressure as well as with decreasing pressure.
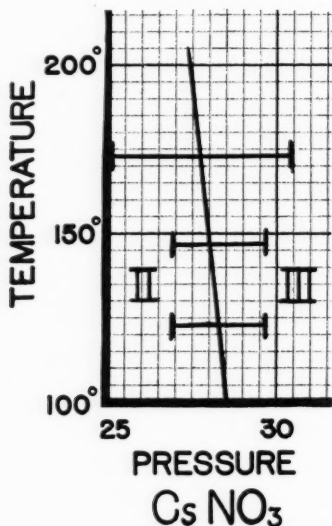

FIGURE 24. The high pressure transition line of $CsNO_3$; Centigrade temperature against pressure in thousands of kg/cm².

The other high pressure transition, II–III, has a volume change of the order of only a third of that of III–IV, but it is still large enough to be comfortably measurable except for the fact that the pressure of the transition is so near to that of III–IV that it is not easy to separate completely the two transitions. At first measurements were made successively on the two transitions, but this was not particularly satisfactory, and the transition II–III was finally studied by itself, taking care not to raise the pressure high enough to start the transition to IV. The sluggishness of the transition II–III rapidly becomes greater at lower temperature; this made impractical the

isolated measurement of II–III below 50° C. At the higher tempera-
tures the sluggishness disapppears, while that of III–IV does not;
this made it feasible to follow the transition II–III to somewhat
higher temperatures than III–IV.

At the higher temperatures, where the transitions run rapidly,
the results were clean cut and satisfactory. At lower temperatures,
that is, 50° or less, the situation is much less clear. On at least three
occasions at room temperature and 50° irregularities were found
larger than the usual experimental error, but not certainly larger
than possible error, which strongly suggested other transitions.
These effects could not be repeated. This, however, is not definite
evidence. Phenomena of suppression and transgression may be
particularly prominent with $AgNO_3$. Thus on one occasion the
modification II was held at room temperature at approximately 20,000
kg/cm^2 for 42 hours. It had then apparently lost the capacity to
change to either of the high pressure modifications, two excursions to
the maximum pressure at 60° not giving any transition at all. The
ability to change to III and IV was restored at 120°. It is almost
certain that there must be other transitions at lower tenperatures.
The location of the transition at solid CO_2 temperature is itself
strong presumptive evidence for this, because abnormal curvature
would be demanded of either the I–II or the II–III line to reach this
point. In addition, there is the change of volume, which is too large
for either I–II or II–III. But perhaps the most convincing evidence
is the velocity of the transition, which was unexpectedly large, cer-
tainly very much larger than could be expected by any extrapolation
from the results on the line II–III. On the other hand, there are
irregularities in the transition velocity on the line I–II pointing to
something more complicated. Figure 25 shows that the width of the
region of indifference is greater at room temperature than at 50°.
In my previous work abnormal variations were found in the transi-
tion velocity near 0°. In Figure 25 the small circles indicate the
coordinates of I–II previously found. There is failure of agreement
at the lower temperatures. All things considered it seems to me that
the most probable interpretation is that there are at least two new
modifications with transition lines running somewhere in the region
suggested by the dotted lines in Figure 25. The change of volume
must be almost all carried by the transitions meeting near CO_2 tem-
perature, because the measured change of volume at this point is
approximately the sum of I–II and II–III. In addition to the transi-
tions indicated, it is not altogether unlikely that there may be a
transition with very small change of volume and approximately

horizontal transition line running across the II region of the diagram between room temperature and 60°. Further experimental study
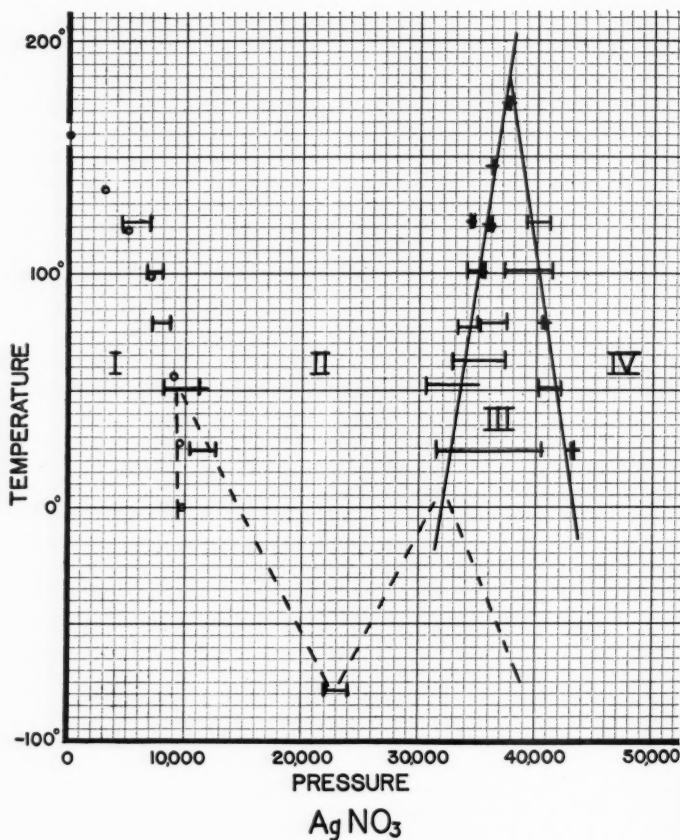

FIGURE 25. The phase diagram of AgNO₃; Centigrade temperature against pressure in thousands of kg/cm². The circles show the previously determined coordinates, and the dotted lines suspected new transitions.

of the questions raised here would demand a considerable modification in the apparatus in order to permit the control of temperatures between room temperature and the CO_2 point.

The results are shown in Figures 25 and 26, and the values of the transition parameters that can be established with confidence in Table IX.   The data for I–II have been given in the previous paper,
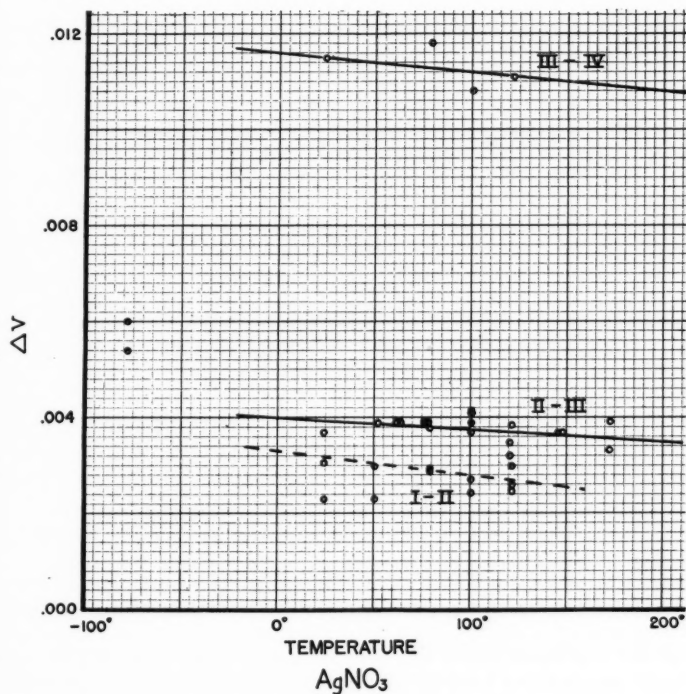

FIGURE 26.   The volume change of the transitions of AgNO$_3$ in cm^3/gm against Centigrade temperature.

and are doubtless more accurate than those found here, which are sufficiently well reproduced in the figures.

TABLE IX

TRANSITION PARAMETERS OF AgNO₃

Pressure kg/cm²	Temperature °C.	$\frac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
		II–III			
32,000	0	.0333	.00400	32.8	0.77
33,500	50	.0333	.00388	37.7	0.88
35,000	100	.0333	.00375	42.0	0.98
36,500	150	.0333	.00363	46.1	1.08
38,000	200	.0333	.00350	49.7	1.17
		III–IV			
43,200	0	−.0333	.0116	95.	2.23
41,700	50	−.0333	.0114	111.	2.60
40,200	100	−.0333	.0112	126.	2.94
38,700	150	−.0333	.0110	140.	3.27
37,200	200	−.0333	.0108	153.	3.60

NaClO₃. The shearing curve of this substance has an abrupt drop in the neighborhood of 39,000, suggesting a transition. Nine different runs were made with the volume apparatus, all with one filling and without accident, at various temperatures from − 80° to 170°. There are three new high pressure modifications; the phase diagram is not unlike that of KCN.

The experimental points are shown in Figures 27 and 28, and the transition parameters in Table X. The parameters given are in some cases rather rough, and must not be extrapolated beyond the limits given. For example, if the difference of volume between II and III were extrapolated linearly with temperature it would change sign in the neighborhood of 50°, an absurd result. The actual curves for Δv must depart considerably from linearity, as do probably also the pressure-temperature curves.
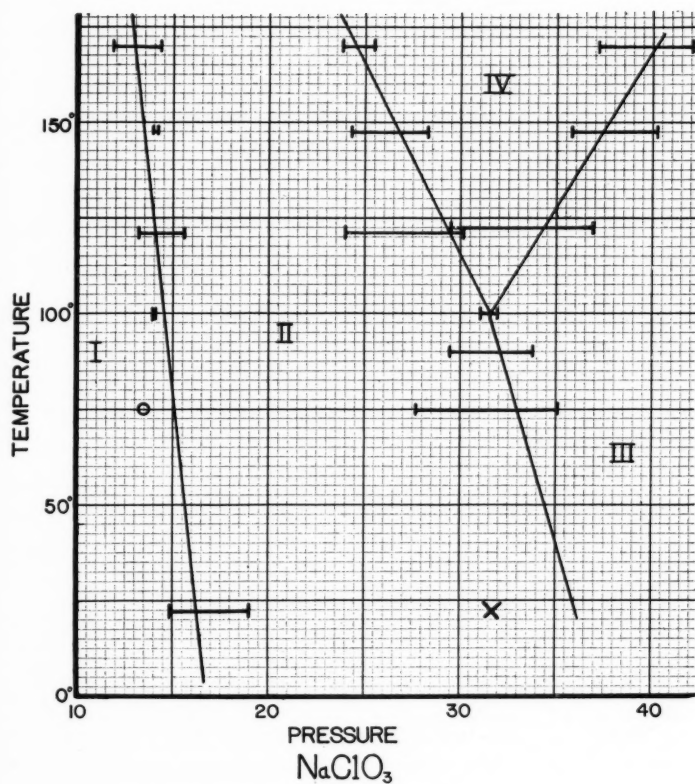
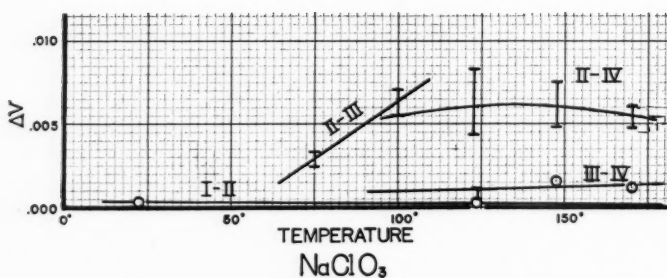FIGURE 27. The phase diagram of NaClO₃; Centigrade temperature against pressure in thousands of kg/cm².

FIGURE 28.   The volume change of the transitions of NaClO₃ in cm³/gm
against Centigrade temperature.

TABLE X

TRANSITION PARAMETERS OF NaClO₃

Pressure kg/cm²	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
			I–II		
16,300	20	−.0455	.00035	2.25	.053
15,200	70	−.0455	.00028	2.11	.050
14,100	120	−.0455	.00020	1.73	.041
13,000	170	−.0455	.00013	1.26	.030
			II–III		
33,100	75	−.0157	.0030	66.	1.56
31,500	100	−.0157	.0065	154.	3.62
			II–IV		
31,500	100	−.0102	.0055	201.	4.71
28,070	135	−.0102	.0061	250.	5.86
24,640	170	−.0102	.0055	239.	5.60
			III–IV		
31,500	100	+.00796	−.0010	46.9	1.10
35,900	135	+.00796	.0012	63.0	1.47
40,290	170	+.00796	.0014	77.9	1.83

TRIPLE POINT II–III–IV

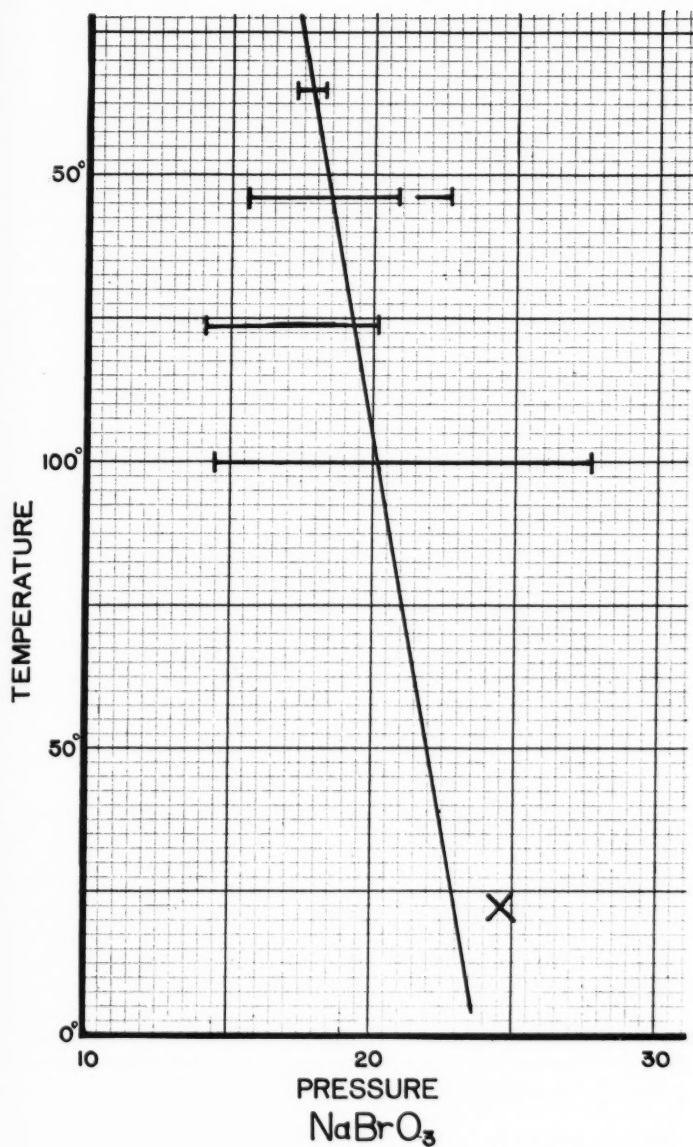|					
	II–IV	−.0102	.0055	201.	4.71
31,500	100 III–IV	+.00796	−.0010	47.	1.10
	II–III	−.0157	.0065	1.54	3.62

FIGURE 29. The transition of NaBrO₃; Centigrade temperature against pressure in thousands of kg/cm².

The triple point II–III–IV affords an interesting example of the way in which the speed of a transition increases and the width of the band of indifference decreases as the triple point temperature is approached from below.   Figure 27 shows how the band of indifference between II and III has almost vanished at the triple point temperature, whereas at a temperature only a few degrees higher, where the transitions II–IV and IV–III replace II–III the transitions have again become sluggish, with wide band of indifference, which becomes less as temperature rises.
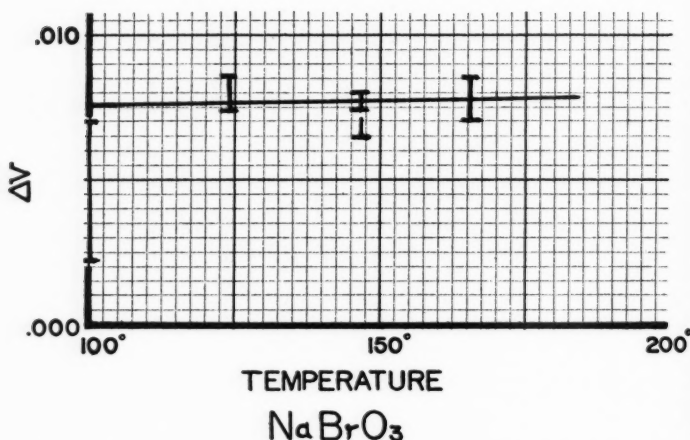

FIGURE 30.   The volume change of the transition of NaBrO₃ in cm³/gm against Centigrade temperature.

NaBrO₃.   This was "c.p." stock from Eimer and Amend.   The shearing curve has a rather sharp knee at 26,000, at which the character of plastic flow abruptly changes from noisy and snapping to quiet.   A transition might be suspected at such a point, but other cases have been found of similar behavior in shear with no transition.

The measurements in the volume apparatus disclosed one new high pressure form with a rather large change of volume.   Seven different runs were made from CO_2 temperature to 170°, with two different fillings of the apparatus.   Measurements with the first filling were terminated by an explosion.   The transition has a high temperature coefficient of activity; at CO_2 and room temperatures it is so sluggish
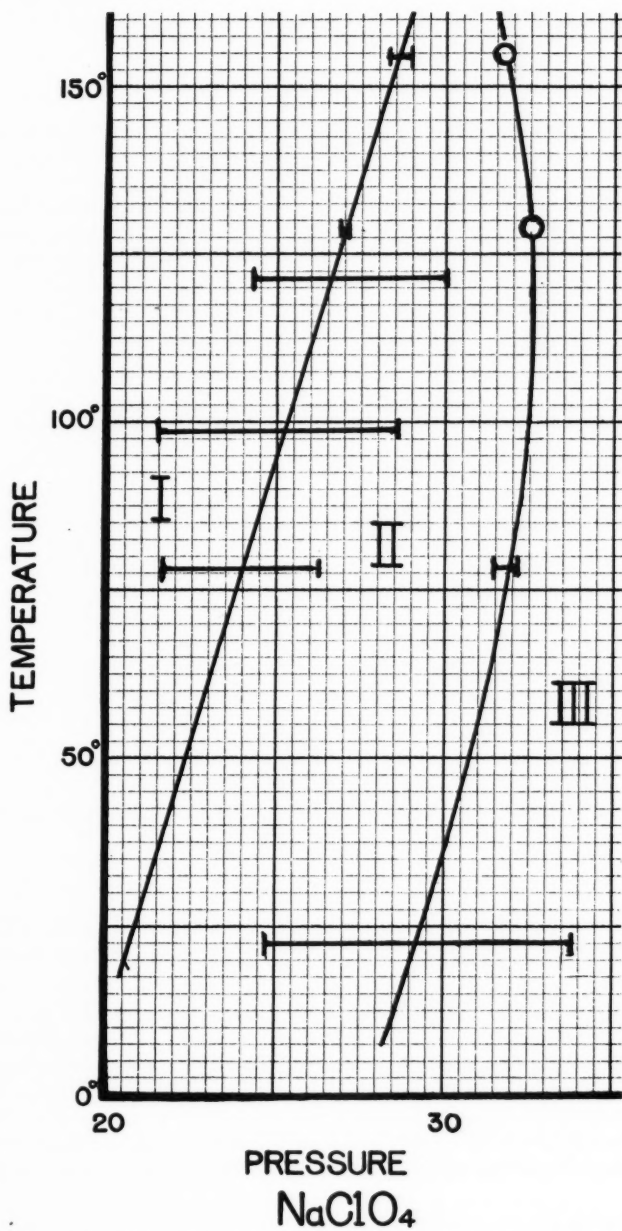
FIGURE 31.   The phase diagram of NaClO₄; Centigrade temperature against pressure in thousands of kg/cm².

that nothing definite could be established.   At 100° the width of the
band of indifference is about 16,000 kg/cm²; above 100° the width
becomes less, nearly vanishing at 170°.

   The experimental values are shown in Figures 29 and 30, and the
parameters in Table XI.   It is obvious from the figure that both
transition curve and change of volume have considerable uncertainty.

<div align="center">TABLE XI</div>

<div align="center">TRANSITION PARAMETERS OF NaBrO₃</div>

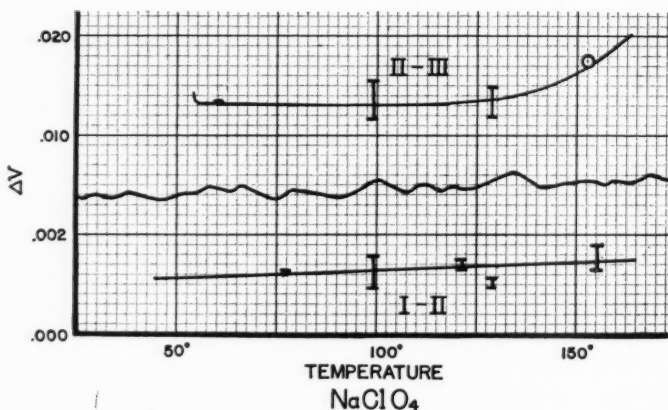| Pressure kg/cm²	Temperature °C.	$\dfrac{dz}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
20,200	100	−.027	.0076	105	2.4$_6$
18,900	135	−.027	.0077	116	2.7$_3$
17,600	170	−.027	.0078	128	3.0$_0$

FIGURE 32.   The volume change of the transitions of NaClO₄ in cm³/gm
against Centigrade temperature.   Notice the change of scale for the two
transitions.

NaClO₄.   The material was "c.p." stock from Eimer and Amend.
The shearing curve had one inconspicuous upward break at 37,000,
and another exceptional point at 25,000 where the character of the
plastic flow changed from smooth to scratchy, but without noticeable
change in slope, so that perhaps two transitions would be suggested,
although one would not have felt great confidence in this prediction.
Two new phases were as a matter of fact found with the volume

apparatus. Seven runs were made in all with a single filling, without accident, in the temperature range from − 80° to 155°.

The experimental results for transitions curves and change of volume are shown in Figures 31 and 32, and the calculated transition parameters in Table XII. The high pressure transition II–III runs readily at the higher temperatures, and with so large a change of volume that equilibrium readings could be obtained with both phases present. There seems to be no question but that the transition line II–III deviates markedly from linearity.

TABLE XII

TRANSITION PARAMETERS OF NaClO₄

Pressure kg/cm²	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
			I–II		
22,300	50	.0167	.00115	22.3	.52
25,300	100	.0167	.00132	29.5	.69
28,300	150	.0167	.00148	37.5	.88
			II–III		
29,000	20	.0182			
31,000	60	.0227	.0134	197	4.6
32,500	100	.0454	.0131	108	2.5
32,600	130	−.0909	.0136	−60	−1.4
31,500	160	−.0130	.0190	−633	−14.8

In addition to the transitions given there is some very doubtful evidence for a transition with very small volume change in the region around 150° and 10,000 kg/cm².

NaIO₄. This was obtained from Mackay. The shearing curve was normal enough, with no suggestion of a transition.

With the volume apparatus a small transition was found, of such characteristics that it is difficult to establish the parameters with any accuracy. Runs were made at room temperature, 125°, and 150°, with two different fillings of the apparatus. With increasing pressure the transition runs so sluggishly and with such small volume change that one could not be sure of even the existence of the transition. With decreasing pressure, however, there is an abrupt discontinuity of volume, but of such small magnitude that no equilibrium setting with both phases could be attempted. This discontinuity on decreasing pressure was definitely established at approximately the same pressure at each of three runs at 125°. At room temperature it was not found, because of too great sluggishness probably. At 150° fairly

good evidence of the discontinuity was also obtained, but with some uncertainty due to leak in the absolute gauge with which the hydraulic press was controlled. This was a new type of gauge under trial, and was used for this one run only.

The pressure of volume discontinuity with decreasing pressure was 9,000 kg/cm² at 125° and 25,000 at 150°. Since the transition with increasing pressure could not be located, it is not possible to guess how wide the region of indifference is and hence to estimate what the true equilibrium pressures are at these temperatures. It is probable, however, that the great difference between the two pressures just quoted cannot be entirely explained by variation of the width of the region of indifference in such a comparatively narrow temperature range, so that it is probable that the transition line runs more nearly horizontally than for most substances. A consequence of this would be that there should be a transition at atmospheric pressure in the neighborhood of 100°.

The volume discontinuity as measured was 0.0010 cm³/gm, consistently for all four measurements. It is not possible to tell how close this is to the volume change at the transition itself, since a difference of compressibility of the two phases, combined with the fact that the pressure of discontinuity may have been some distance from the true equilibrium pressure, would falsify the true change of volume. It is probable, however, that this falsification cannot be large because the discontinuity at 150° was so nearly the same as that at 125°, and that 0.0010 is not far from the true volume change of the transition.

In view of the uncertainty of the measurements I have not thought it worth while to give diagrams or tables in greater detail.

KClO₃. This is already known to have a transition,[11] which has been studied to 12,000 kg/cm² with my previous apparatus between 0° and 200°. In the 50,000 apparatus explorations were made to the maximum at CO_2 temperature and 150°. At the lowest temperature the transition apparently starts at 13,000, and continues running all the way to 50,000, pressure being increased at the rate of 2,000 kg/cm² in four minutes. On release of pressure the reverse transition did not start until 1,600 was reached. At 150° the transition ran rapidly, within pressure limits of 700 kg/cm². The mean transition pressure was 7,400 kg/cm² and the mean change of volume 0.027 cm³/gm, against my previous values at this temperature of 7,200, and 0.0248 cm³/gm respectively. No other transition was found up to 50,000. The shearing curve was normal with no indication of a transition.

KIO_4. The material was "c.p." stock from Eimer and Amend. The shearing curve had a minor break downward at 17,000, which of
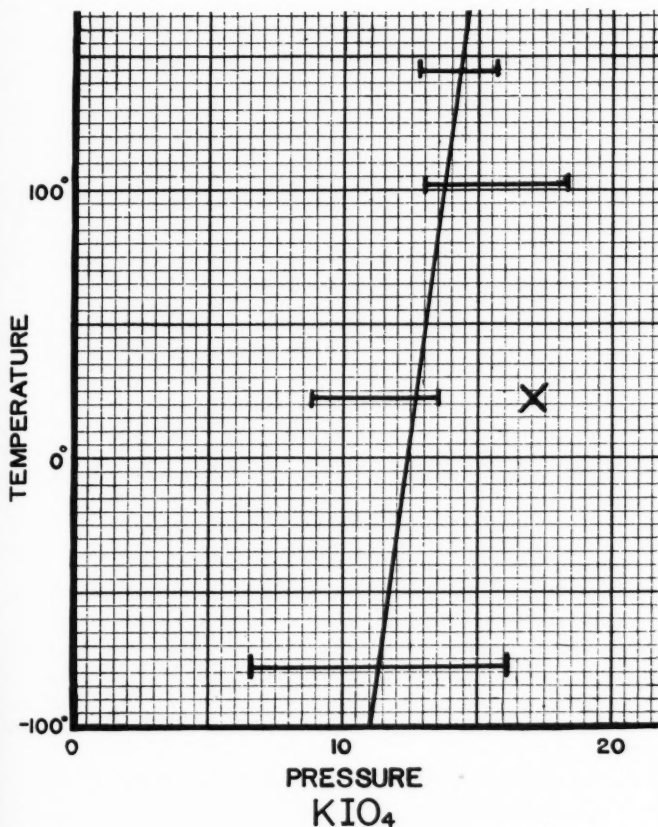

FIGURE 33. The transition line of KIO_4; Centigrade temperature against pressure in thousands of kg/cm². The cross indicates the point of discontinuity of the shearing curve.

itself would probably not have been enough to raise the suspicion of a transition. Four runs were made with the volume apparatus: at

−80°, room temperature, 102°, and 145°, with a single filling and without accident. There is a transition running nearly vertically, with little latent heat, roughly at 12,000 kg/cm². The volume change is not great enough to permit measurements on the two phase system, but once the transition had started, it always ran to completion. The transition is highly unsymmetrical, in that the volume change when
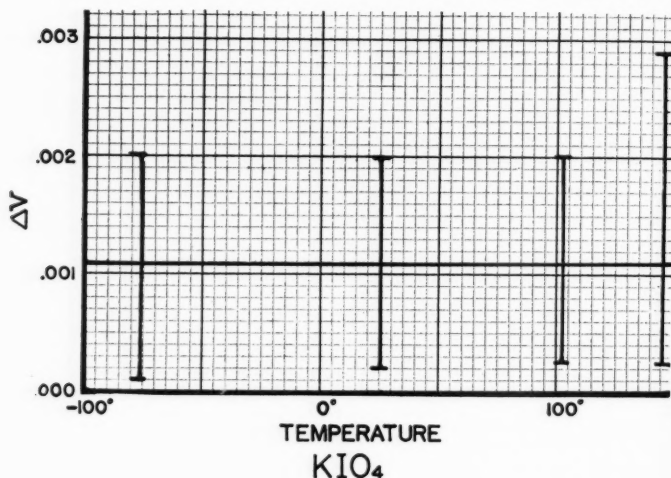

FIGURE 34. The volume change of the transition of KIO₄ in cm³/gm against Centigrade temperature.

the transition runs with increasing pressure is always very much less than when it runs with decreasing pressure. This indicates that the high pressure form is less compressible than the low pressure form; the difference of compressibility is of the order of 2×10^{-7} (kg/cm² units).

The experimental results are shown in Figures 33 and 34, and the transition parameters in Table XIII.

TABLE XIII

TRANSITION PARAMETERS OF KIO₄

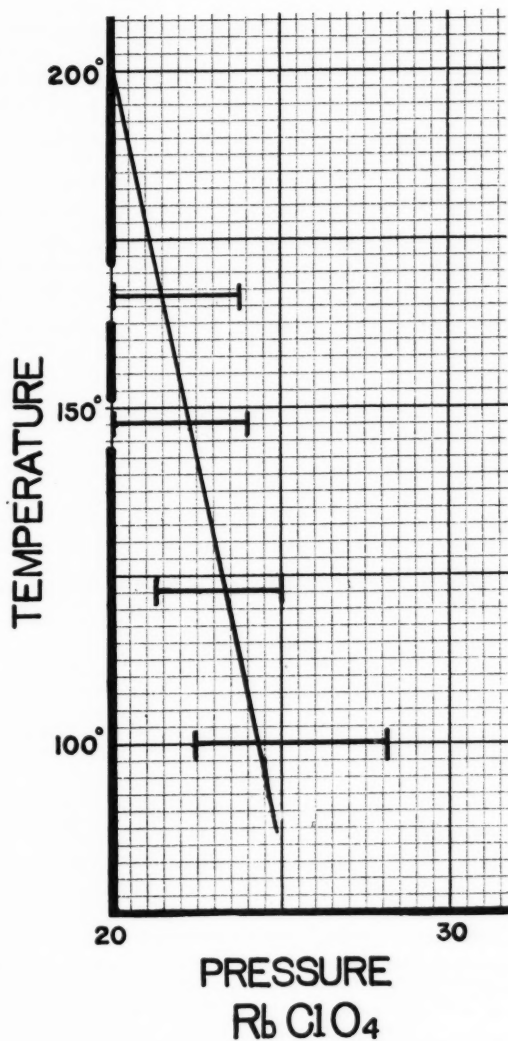| Pressure kg/cm²	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat	
				kg cm/gm	gm cal/gm
11,300	−80	.074	.0011	2.9	.067
12,800	+35	.074	.0011	4.6	.107
14,400	150	.074	.0011	6.3	.148

FIGURE 35. The transition line of RbClO₄; Centigrade temperature against pressure in thousands of kg/cm².

$RbClO_4$. This was obtained from MacKay, made from "c.p." materials by the action of $HClO_4$ on Rb_2SO_4. The shearing curve had a pronounced maximum at 24,000, and a minimum of about one half the maximum at 40,000. A transition is therefore to be confidently expected.
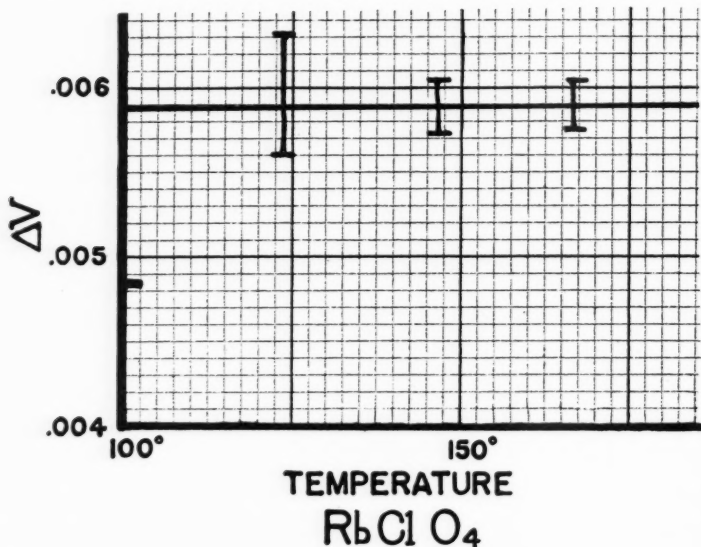

FIGURE 36. The volume change of the transition of $RbClO_4$ in cm³/gm against Centigrade temperature.

Five runs were made with the volume apparatus at temperatures from room temperature to 167° with a single filling of the apparatus without accident. Nothing was found at room temperature out to 50,000. The transition was definitely located at the other temperatures, however, Even at the highest temperatures it is somewhat sluggish, and since the change of volume is not large, it was not possible to obtain equilibrium readings on the two phase system. The experimental points are shown in Figures 35 and 36, and the transition parameters in Table XIV. $RbClO_4$ is known to have a transition at atmospheric pressure at 279°; it seems highly probable that the high pressure modification found here must be new.
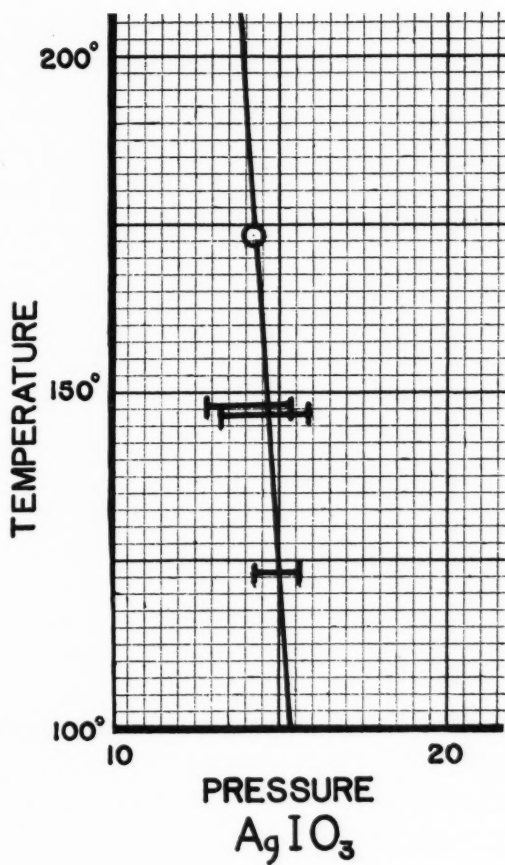
FIGURE 37.   The transition line of AgIO₃; Centigrade temperature against pressure in thousands of kg/cm².

TABLE XIV

TRANSITION PARAMETERS OF RbClO$_4$

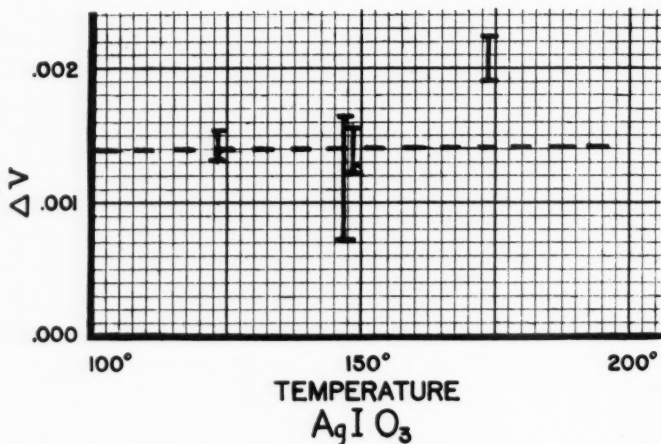| Pressure kg/cm^2	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm^3/gm	Latent Heat kg cm/gm	gm cal/gm
26,300	50	−.0238	.00590	80.1	1.88
24,200	100	−.0238	.00590	92.5	2.17
22,100	150	−.0238	.00590	105.0	2.46
20,000	200	−.0238	.00590	117.4	2.75

FIGURE 38. The volume change of the transition of AgIO$_3$ in cm^3/gm against Centigrade temperature.

AgIO$_3$. This was obtained from MacKay, made from "c.p." chemicals by the action of HIO$_3$ on Ag$_2$CO$_3$. The shearing curve was smooth, with no suggestion of any transition.

With the volume apparatus a transition was found with small change of volume. At room temperature the transition is too sluggish to measure; measurements were made at four temperatures from 123° to 174°. The experimental results are shown in Figures 37 and 38, and the transition parameters in Table XV. The frictional creep with this substance was perhaps somewhat larger than usual, and this introduced some uncertainty into the transition measurements. It is perhaps not entirely ruled out, especially at the higher temperatures that there may be a second transition, close to the one shown.
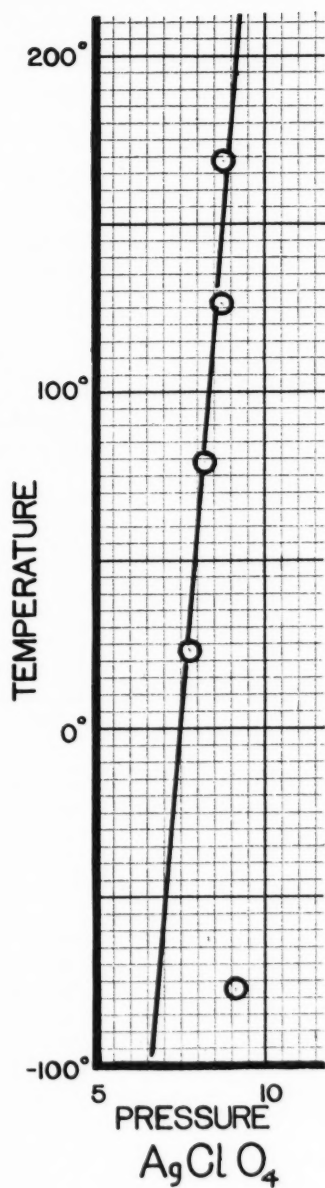
FIGURE 39. The transition line of AgClO₄; Centigrade temperature against pressure in thousands of kg/cm².

TABLE XV

Transition Parameters of $AgIO_3$

Pressure kg/cm²	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
15,300	100	−0.0714	.0014	7.3	.17
14,600	150	−0.0714	.0014	8.3	.19
13,900	200	−0.0714	.0014	9.3	.22

AgClO₄. This was obtained from MacKay, made from "c.p." materials by the action of Ag_2CO_3 on $HClO_4$. As supplied this probably contained free $HClO_4$, which was evaporated off at 130° in vacuum for three hours. The shearing curve was perfectly smooth and gave no evidence of a transition.
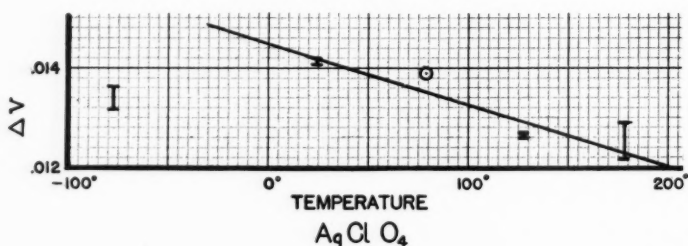

Figure 40. The volume change of the transition of $AgClO_4$ in cm³/gm against Centigrade temperature.

In the volume apparatus there is a transition with large change of volume, so that settings could be made on the two phase system. The transition runs very rapidly, and there was no appreciable region of indifference at any temperature from CO_2 temperature to 169°. The experimental points are shown in Figures 39 and 40, and the transition parameters in Table XVI. The first measurements suggested another transition at CO_2 temperature, but subsequent very careful measurements in the more sensitive apparatus showed nothing not attributable to friction, which sometimes may present puzzling aspects at this low temperature.
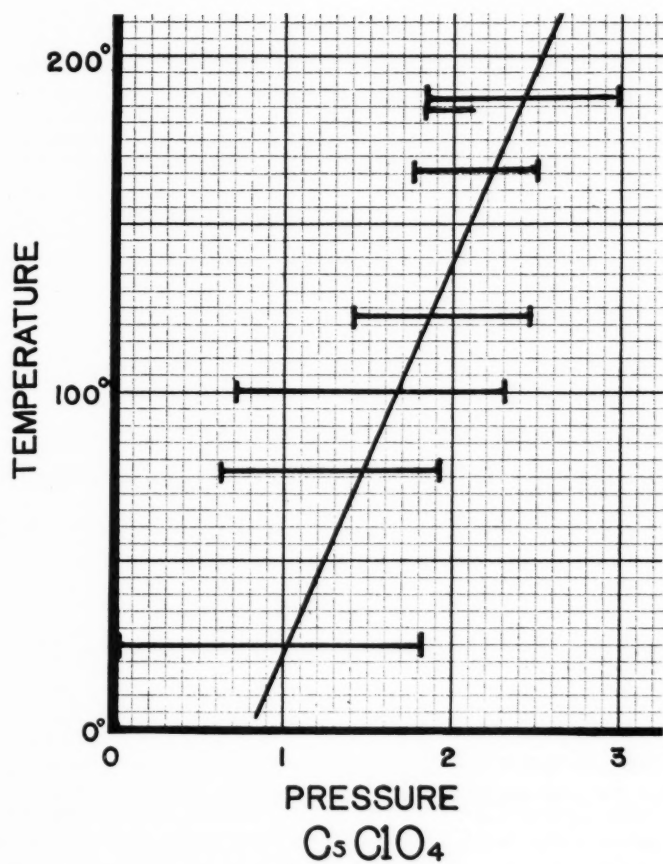
FIGURE 41.   The transition line of CsClO₄; Centigrade temperature against pressure in thousands of kg/cm².

TABLE XVI

Transition Parameters of AgClO₄

Pressure kg/cm²	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
7,500	0	+0.118	.0145	34.1	.80
8,350	100	+0.118	.0132₅	41.9	.98
9,200	200	+0.118	.0120	48.1	1.13

$AgClO_4$ is known to have a transition at atmospheric pressure at 155°. No trace of this was found at 169°, the pressure being too low
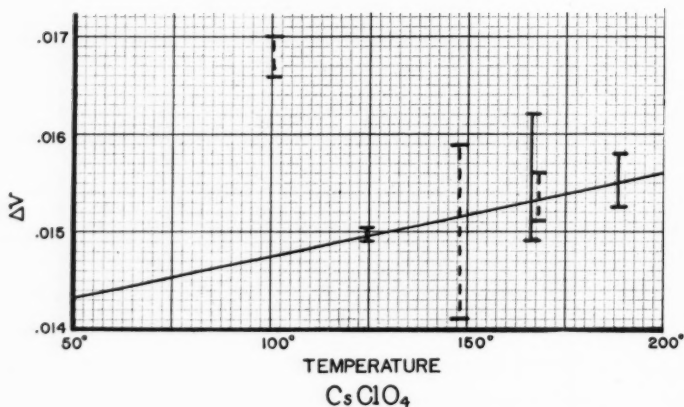

FIGURE 42.   The volume change of the transition of $CsClO_4$ in cm³/gm against Centigrade temperature.

for this apparatus.   In the case of this substance it is obviously possible to say with complete assurance that the high pressure form is different from that previously known at atmospheric pressure at high temperature.   This fact lends plausibility to the assumption that the high pressure forms of the other perchlorates are also different from the known high temperature forms.

CsClO₄.   This material I owe to the kindness of Professor Baxter of the Harvard Chemical Laboratory.   The shearing curve had a gentle upward curvature in the neighborhood of 20,000.   Exploration with the volume apparatus disclosed a transition at very low pressures, so low that accurate measurements could not be made; it is doubtful

whether this transition corresponds to the inflection in the shearing curve. Measurements were made at four temperatures with the regular set-up; no other transitions were found to 50,000. In order to obtain greater accuracy special measurements were made with a special set-up using a piston of 0.375 instead of 0.25 inches diameter, and using about three and a half times as much material as usual. With this apparatus eight runs were made at temperatures between room temperature and 200°. The volume change is so large that equilibrium measurements could easily be made on the two phase system.

The experimental points are shown in Figures 41 and 42, and the transitions parameters in Table XVII.

TABLE XVII
TRANSITION PARAMETERS OF $CsClO_4$

Pressure kg/cm²	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat [kg cm/gm	gm cal/gm
800	0	0.114	.01390	33.3	.78
1,240	50	0.114	.01432	41.8	.98
1,675	100	0.114	.01475	48.3	1.13
2,110	150	0.114	.01517	56.3	1.32
2,550	200	0.114	.01560	64.8	1.52

$CsClO_4$ is known to have a transition at atmospheric pressure at 219°, at which the ortho-rhombic low temperature modification changes to a cubic high temperature modification.

$CsIO_4$. This was obtained from MacKay; it was made from "c.p." materials by the action of HIO_4 on $CsHCO_3$. The shearing curve showed an inconspicuous upward inflection at 38,000 of doubtful significance.

The measurements with the volume apparatus were not as clean cut as could be desired; measurements were made at room temperature 147°, 169°, and 190°. At room temperature nothing definite was found. At the three higher temperatures there is without doubt a transition, but it is sluggish, and the volume change of the pure transition seems to be mixed up with something else, perhaps a slight decomposition. The transition runs at about 6,000 with increasing pressure; the reverse transition is not noticeable until pressure has been reduced back to atmospheric. The best mean of the transition pressures was 3000 kg/cm², independent of temperature. The volume change is of the order of 0.0033 cm³/gm.

$TlClO_4$. This was obtained from MacKay, made from "c.p." materials by the action of Tl_2CO_3 on $HClO_4$. The shearing curve was
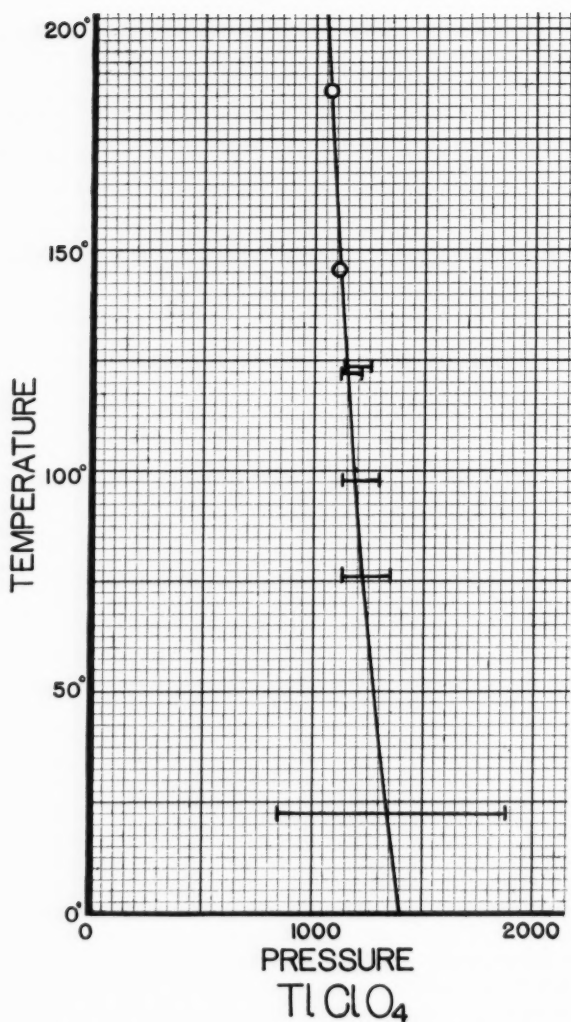
FIGURE 43.   The transition line of TlClO$_4$; Centigrade temperature against pressure in kg/cm^2.

very unusual, having a maximum at 18,000, a minimum at 28,000, and beyond 28,000 rising convex toward the pressure axis. A transition is therefore to be expected.

Seven runs were made in the volume apparatus, with one filling, without accident, at various temperatures from room temperature to 180°. A transition was found with volume change sufficiently large to allow settings on the two phase system at the higher temperatures. At the lower temperatures the transition becomes very sluggish, and the band of indifference wide.
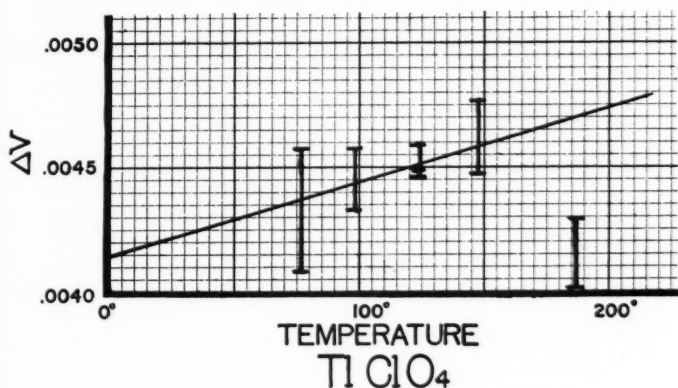

FIGURE 44. The volume change of the transition of TlClO$_4$ in cm^3/gm against Centigrade temperature.

The experimental points are shown in Figures 43 and 44, and the transition parameters in Table XVIII. This substance is known to have a transition at atmospheric pressure at 266°. It is highly improbable that the transition line found here cuts the temperature axis at this temperature, so that it is probable that this high pressure phase is new.

TABLE XVIII

TRANSITION PARAMETERS OF TlClO$_4$

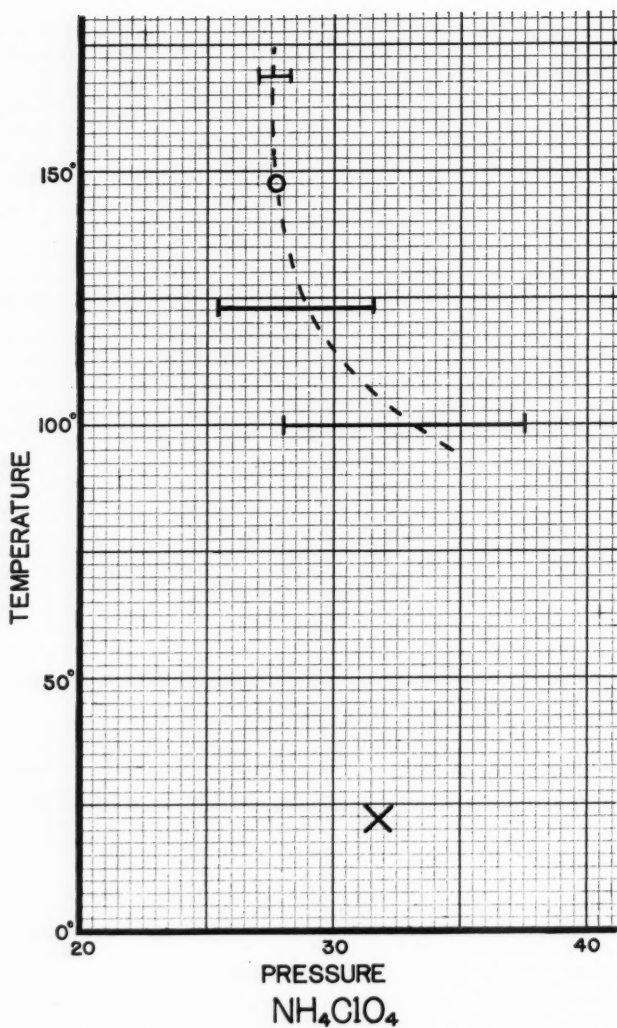| Pressure kg/cm^2	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm^3/gm	Latent Heat	
				kg cm/gm	gm cal/gm
14,000	0	−.0715	.00414	15.8	.370
12,800	50	−.0962	.00429	14.4	.337
11,900	100	−.1250	.00444	13.2	.311
11,200	150	−.1587	.00459	12.2	.287
10,600	200	−.2000	.00474	11.2	.263

FIGURE 45. The transition line of NH_4ClO_4; Centigrade temperature against pressure in thousands of kg/cm^2. The cross marks the point of discontinuity in the shearing curve.

NH₄ClO₄. This was fresh "c.p." stock from Eimer and Amend. The shearing curve had a maximum of cusp-like sharpness at 31,000 Four runs were made with the volume apparatus with a single filling without accident, from room temperature to 168°. The change of volume is too small to permit determinations of equilibrium with both phases present.
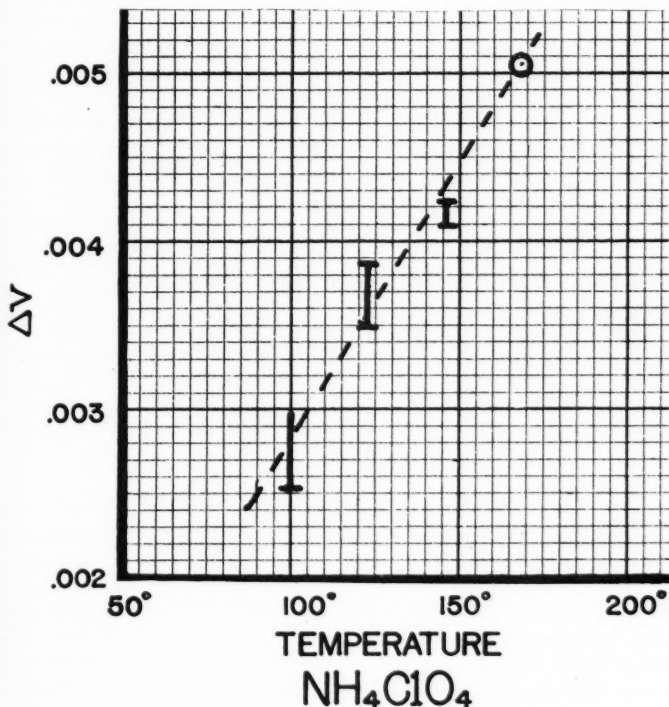

FIGURE 46. The volume change of transition of NH₄ClO₄ in cm³ gm against Centigrade temperature.

The experimental results are shown in Figures 45 and 46. The uncertainty in the transition curve due to the wide region of indifference is too great to permit computing a table of parameters, which can be obtained from the figures with all the accuracy warranted.

In spite of the insensitiveness of the measurements, however, this substance seems to be highly unusual. Δv falls off with decreasing temperature at a roughly linear rate and so rapidly that it should vanish at some temperature not far from $0°$. The transition line is curved in a direction consistent with this. If the line continues with the same curvature it will have a horizontal tangent at the point at which Δv vanishes. This would be the only example of a transition curve with a minimum; HgI_2 has a curve with a maximum. The evidence from the shearing curve is not favorable to this interpretation, which would demand an abnormally large displacement of equilibrium pressure with shear. It is perhaps not unreasonable to suppose that the maximum of the shearing curve is concerned with still another modification, and that the apparent progress of the transition line of Figure 45 toward a minimum will be arrested by a transition line and the appearance of a new phase.

Na_2SO_4. This substance is known to be complexly polymorphic at atmospheric pressure, at least five modifications being recognized, one of which is metastable.[12] The transitions all occur above $160°$. In general they are characterized by unusual sluggishness and capacity for superheating or subcooling. The shearing curve at room temperature showed no indication of a transition, the curve being entirely normal, concave toward the pressure axis, with rather well marked knee. Six runs were made in the volume apparatus, with a single filling, without mishap. The first run at room temperature yielded no obvious transition; the remaining five runs were spaced between $100°$ and $175°$.

An ice type transition was picked up at $147°$ and $100°$. This is very sluggish; at $100°$ it runs with appreciable velocity with increasing pressure at $21,000 \ kg/cm^2$, and the reverse transition does not run with appreciable velocity until atmospheric pressure is reached. At $147°$ appreciable velocity with increasing pressure was not reached below $14,500$, where the transition ran to completion. On decrease of pressure it is probable that the transition did not run to completion at any pressure, restoration of the initial condition being brought about only by decrease of temperature. At $100°$ good values for the change of volume were found both with increasing and decreasing pressure. These two values were exactly the same, indicating that the two phases have sensibly the same compressibility. The identification of this transition with one of those studied by Kracek and Gibson is made possible by the change of volume, which corresponds to the transition IV–III (rather than the metastable change V–III).

The volume change decreases somewhat with increase of temperature, as it normally does with this type of transition.

In addition to the known transition IV–III, another transition III–VI was found at high pressures, the new phase not being capable of existence at atmospheric pressure. This transition, like the other, is characterized by sluggishness and wide limits of indifference. Furthermore, the transition velocity is unsymmetrical on the two
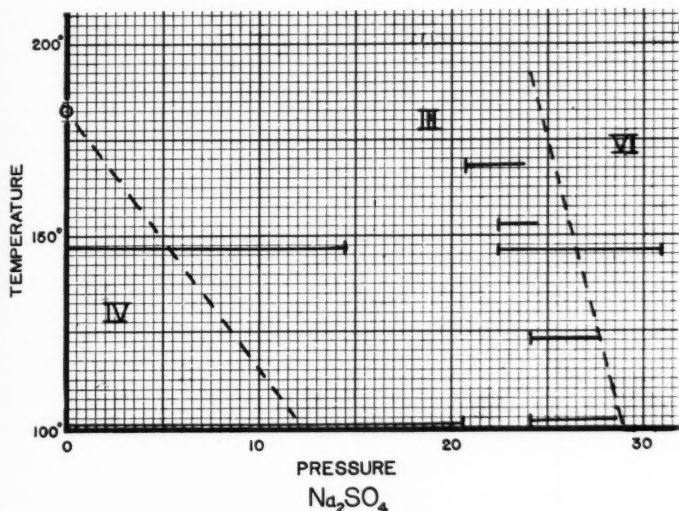

FIGURE 47. Part of the phase diagram of Na_2SO_4; part of the diagram at higher temperatures has been established by Kracek. Centigrade temperature is plotted against pressure in thousands of kg/cm².

sides of the transition line. With increasing pressure the transition is spread through a considerable pressure range and runs so slowly that satisfactory evidence of its existence with increasing pressure was obtained only once, at 31,000 kg/cm². However, after application of 50,000 kg in 2,000 intervals on the regular two minute schedule the transition seems to be completed, and on release of pressure discloses itself much more definitely than with increasing pressure, satisfactory evidence of its existence having been found on five different occasions. The change of volume is smaller than for the

transition III–IV, being of the order of 0.002 cm³/gm; this again decreases with increase of temperature.

The experimental values of transition pressure and temperature and of change of volume are shown in Figures 47 and 48. The values are not accurate enough to justify an attempt to compute the latent
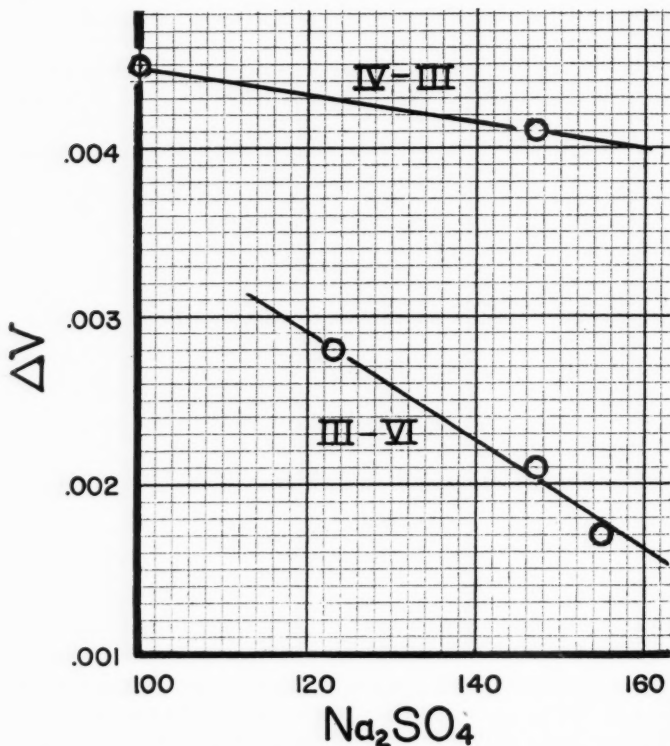

FIGURE 48.   The volume change of two of the transitions of Na₂SO₄ in cm³/gm against Centigrade temperature.

heat.   It is probable that the transition III–VI is also of the ice type, but rising much more steeply with temperature, and therefore with a smaller latent heat than III–IV.   From Kracek and Gibson's latent

heat the slope of the transition line III–IV may be computed by Clapeyron's equation; this line is shown dotted in Figure 47.   It is seen to be at least consistent with the very wide limits found above for the transition.

$KMnO_4$.   The material was old laboratory stock.   The shearing

FIGURE 49.   The phase diagram of $CsMnO_4$; Centigrade temperature against pressure in thousands of kg/cm².

curve showed a very pronounced upward break at 20,000 kg/cm², strongly suggesting a transition.   Four runs were successfully made with a single filling of the volume apparatus, twice at room temperature and twice at 100°.   There is a transition, but the volume change is very small, and accurate results were not possible.   The transition line runs nearly vertically, and therefore with little latent heat, at a pressure of 16,000 kg/cm².   The volume change is of the order of 0.0007 cm³/gm.   The high pressure modification appears to be less compressible than the low pressure modification.

CsMnO₄. This material had been prepared by Dr. J. O. Morrison of Williams College in 1932. It has been kept sealed and in the dark since then. I am indebted to Professor H. E. Bent of the Harvard Chemistry Department for telling me of the existence of this material and procuring it for me. The shearing curve was of the normal con-

FIGURE 50. The change of volume of the transitions of $CsMnO_4$ in cm³/gm against Centigrade temperature.

cave shape toward the pressure axis up to about 30,000 kg/cm². At this pressure there was a definite break upward, suggesting a transition.

Measurements were made in the volume apparatus at five temperatures from CO_2 temperature to 168°. There are two transitions, one at comparatively low and the other at high pressures. At CO_2 temperature the transition was too sluggish to permit quantitative measurements, but there was enough creep during release of pressure to indicate that the high pressure transition had run during increase of pressure to a certain extent. The change of volume of both transitions is fairly large, and at the higher temperatures fairly definite equilibrium settings could be obtained. The change of volume of the

high pressure transition is made somewhat uncertain by the fact that the pressure is so high that during increase of pressure it was impossible to disentangle the transition from creep in the apparatus. The changes of volume of the same transition obtained with decrease of pressure suffer from uncertainty as to whether pressure had been held at the maximum long enough to permit the transition to run to completion. The changes of volume at the two highest temperatures, where the transition runs most rapidly, should have the least error from this source.

The experimental points are shown in Figures 49 and 50 and the transition parameters in Table XIX.

TABLE XIX

TRANSITION PARAMETERS OF CsMnO₄

Pressure kg/cm²	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
		I–II			
16,200	0	−0.0303	.0080	72.0	1.69
14,550	50	−0.0303	.0071	75.6	1.77
12,900	100	−0.0303	.0062	76.4	1.79
11,250	150	−0.0303	.0054	75.4	1.76
9,600	200	−0.0303	.0045	70.3	1.65
		II–III			
41,600	0	−0.0477	.0133	76.0	1.78
40,550	50	−0.0477	.0134	90.7	2.13
39,500	100	−0.0477	.0135	105.6	2.47
38,450	150	−0.0477	.0136	120.6	2.83
37,400	200	−0.0477	.0137	135.4	3.18

$Pb(C_2H_3O_2)_2$, anhydrous. The material was "tested purity" stock from Eimer and Amend, dehydrated by heating to 130° in vacuum. The shearing curve showed a sharp upward break at 26,000 kg/cm², leading to the expectation of a transition.

The transition exploration with the volume apparatus was made with three different set-ups, one with the regular apparatus to a maximum pressure of 51,000, and two with the larger apparatus used when more sensitive measurements are required at lower pressures to a maximum of 23,000. The evidence seems unmistakable that there are three new modifications. The volume changes are small, however, and in some parts of the diagram the transitions are more than usually sluggish, so that it was not possible to get as satisfactory values for the parameters as usual.

The experimental points are shown in Figures 51 and 52, and the

transition parameters are collected in Table XX. It is obvious
enough from the figures that there is considerable uncertainty with
regard to the precise numerical results. The transition lines I–II

FIGURE 51. The phase diagram of $Pb(C_2H_3O_2)_2$; Centigrade temperature
against pressure in thousands of kg/cm^2.

and II–III have been drawn straight in the figure. This demands
that there be transitions at atmospheric pressure not apparently
noted in the literature. It is not at all ruled out that these transition
lines are actually curved in such a way that they never cut the axis of
atmospheric pressure. If this is the case, the modification called III

in the diagram is the modification normally encountered at atmospheric pressure. The precise location of the line I–IV is also in considerable doubt because of the unusual way in which the breadth of the region of indifference varies with pressure and temperature, although this is not without precedent. At 143° the transition was not detected out to 45,000 kg/cm² , doubtless because of too great sluggishness.

FIGURE 52. The volume change of the transitions of $Pb(C_2H_3O_2)_2$ in cm³/gm against Centigrade temperature.

TABLE XX

TRANSITION PARAMETERS OF $Pb(C_2H_3O_2)_2$

Pressure kg/cm²	Temperature °C.	$\dfrac{d\tau}{dp}$	ΔV cm³/gm	Latent Heat kg cm/gm	gm cal/gm
		I–II			
0	20	.026	.0082	92.	2.2
5,000	150	.026	.0075	121.	2.8
		II–III			
0	50	.030	.0048	52.	1.2
5,000	200	.030	.0043	68.	1.6
		I–IV			
10,500	0	.0286	.0015±	140.	3.4
14,000	100	.0286	.0015±	200.	4.6

Substances Giving Negative Results

In addition to the 35 substances just enumerated with transitions large enough to measure, a number of other substances were examined for new transitions with negative results. These substances were selected for one or another reason. In a number of instances there were breaks in the shearing curves which suggested a transition. Since the general character of the shearing curves of all these substances has been summarized in another paper on the general subject of shearing phenomena, it is not necessary to reproduce these shearing results here. The number of instances was comparatively small in which the shearing curves suggested transitions which were not found in the volume apparatus. In the majority of cases in which new forms were found not suggested by the shearing curves the existence of a new modification was suspected because of the chemical similarity of the substance to some other which was known to be polymorphic. The number of substances listed as polymorphic will depend importantly on the sensitiveness of the method in detecting small volume changes, for there seems to be no predeliction for the volume changes of those transitions which have been measured to cluster around any special magnitude. Doubtless a more enthusiastic interpretation of small irregularities in some of the curves would have swelled the list of substances called polymorphic, but I have preferred to put the doubtful cases in almost every instance on the negative side. The general order of magnitude of a volume discontinuity which can be surely established is suggested by the smallest values already tabulated. Some substances are more favorable in this respect than others, the regularity of the volume measurements depending on the internal friction.

In the following, unless otherwise noted, the exploration which yielded negative results was made out to 50,000 kg/cm² at room temperature and at 150° C. The arrangement in the following is alphabetical, according to the metal in the salt.

Ammonium. NH_4IO_3 and NH_4IO_4 definitely negative. NH_4NO_3 gave irregularities at 150° between 10,000 and 20,000 which are probably due to the transitions already known, but the possibility of new transitions is not entirely ruled out.

Antimony. $SbBr_3$. This was tried because of its abnormally low melting point and unusual mechanical softness.

Barium. BaS, tried only at room temperature to 39,000 kg/cm².

Bismuth. $BiCl_3$; Bi_2S_3; Bi_2O_3. The two latter have shearing curves with very pronounced maxima, which must mean something drastic.

Since no polymorphic transition could be found in the volume apparatus, the interpretation of the shearing curve as indicating a decomposition to the metal is strengthened.

Cadmium. $CdBr_2$.

Caesium.   CsF; my expectation was strong that this would assume a body centered arrangement at high pressures like the other halogen compounds, but nothing was found at room temperature or 130° to 57,000. $CsClO_3$, $CsBrO_3$, $CsIO_3$, all gave negative results.   Three different set-ups were made with $CsBrO_3$; this experiences some sort of an irreversible volume change at low pressures at 150°.   X-ray analysis by Dr. Jacobs showed no detectible alteration in the lattice. Perhaps a small amount of moisture may have been responsible.

Chromium.   Chrome alum, plus water of crystallization.   Examined to 50,000 at room temperature, and at 75° to only 20,000, where the cylinder ruptured.

Copper.   CuS; Cu_2S.   The latter gave nothing at either temperature.   The former gave nothing at room temperature, but at 150° appeared to have a transition between 2000 and 4000.   However, the texts on chemistry emphasize the difficulty of getting the sulfides pure, and since no transition is recorded in the literature at atmospheric pressure, and NiS, which I had obtained from the same chemical supply house, was very definitely not chemically homogeneous, I did not pursue the matter further because of the probability of getting into unwelcome chemical complications.

Lead.   PbSe; the shearing curve has a very strong maximum, but the results with the volume apparatus were entirely negative, suggesting a decomposition under shearing stress.   PbTe, gives also a maximum in shear, but is negative in the volume apparatus. $Pb_3(PO_4)_4$ was examined twice; there is an irreversible permanent change of volume at low pressures at 150°, for which no evidence could be found by Dr. Hultgren on X-ray analysis. $2PbCO_3.Pb(OH)_2$. $Pb(C_2H_3O_2)_2$ $3H_2O$ gave negative results, although the anhydrous salt has four modifications.

Lithium. Li_2SO_4: highly unusual shearing curve; surprising that no new modification was found.

Manganese. Mn_3O_4.

Mercury. $HgSO_4$, Hg_2Cl_2, HgI.   Almost certain that these decompose to metallic mercury in shear.

Nickel.   NiS.   Irreversible changes at low pressures at 150° doubtless due to imperfect purity.

Potassium. $KBrO_3$.   Much time was spent on this compound, the appearance being that of a very sluggish transition spread over a wide

pressure range. The evidence did not prove convincing, however, and I list it as negative. KIO_3, $KClO_4$, KNO_3.

Rubidium. $RbClO_3$, $RbBrO_3$, $RbIO_3$, $RbIO_4$.

Silver. Ag_2SO_4; the shearing curve is highly unusual, running horizontally from 15,000 to 33,000, then falling to a minimum at 45,000 and rising again. Volume explorations were made at solid CO_2 temperature, room temperature, and 150°. There are indications of a transition line running nearly vertically in the neighborhood of 15,000, but I could not establish it certainly. $AgBrO_3$. $AgIO_4$; in addition to the run at room temperature, two runs were made at 150° and one at 200°. At the two higher temperatures there is some sort of a volume change below 4000 kg/cm^2 which is at least partially reversible. However, no simple interpretation of the results was evident, and I did not pursue the matter further. $AgClO_3$.

Sodium. NaF; the shearing curve definitely has a maximum near the end of the pressure range, leading to the expectation of a transition. Because of the interest which any transition in this particularly simple compound would have, unusually careful exploration was made with the volume apparatus. Two set-ups were used; with the second set-up runs were made at 25°, 125°, 150°, and 175°. At first it appeared that there was a small break with decreasing pressure at pressures so high that the effect could not be certainly disentangled from creep in the apparatus, but more careful measurements showed nothing that was not certainly due to frictional irregularities at the highest pressures. In any event it is certain that there is no transition with the large volume change associated with the change from face centered to body centered, which is the transition anticipated. $NaCl$, NaI; again the change from face centered to body centered was anticipated, particularly because of the behavior of the potassium and rubidium salts, but none was found. The chances were probably best for finding it with NaI. $NaIO_3$, $NaCN$, $NaNO_3$, $NaSCN$. Particularly careful search was made with the latter, since irregularities on the first set-up indicated a possibility at low pressures. Repetition with the more sensitive apparatus at 175° gave nothing.

Strontium. SrO, $SrBr_2$, SrS, $SrSO_4$.

Thallium. $TlClO_3$, explodes at 150° at atmospheric pressure; repetition at 125° gave nothing. $TlBrO_3$, explodes at atmospheric pressure at 140°; repetition at 125° gave nothing. $TlIO_3$, negative at room temperature and 125°. $TlIO_4$; the first set-up at four temperatures up to 168° displayed an unexplained creep at low pressures. Repetition at four temperatures up to 125° yielded nothing positive. Tl_2SO_4, $TlNO_3$.

Zinc.   ZnO, ZnS, $ZnSO_4$, $2ZnCO_3 3Zn(OH)_2$.
Zirconium. ZrO_2.

Discussion

The most obvious question for consideration is whether the extension of pressure range from 12,000 kg/cm², the range of my former investigation of polymorphism, to 50,000 discloses any important change in the general character of the phenomena. A graphical summary of my earlier work will be found, for example, on pages 232 and 233 of The Physics of High Pressure. Here are collected the phase diagrams of 36 substances, each diagram in itself being approximately square, the pressure range up to 12,000, as abscissa, occupying the same length as the temperature range, 200°, as ordinate. The rough impressionistic aspect of all these diagrams is of transition lines sweeping over the complete range of both pressure and temperature at approximately 45°. That is, as a very rough average, 12,000 kg/cm² produces a change of transition temperature of the order of 200°. Departures from this rule, of which there are many, are mostly in the direction toward verticality in the lines, that is, a 200° change of temperature for less than 12,000 kg/cm². If now, one plots the new data of this paper in similar square diagrams, the range of abscissas now being 50,000 instead of 12,000 kg/cm², and the temperature range being 200° as before, the impressionistic aspect changes. The transition lines now run approximately vertically across the diagrams. By far the larger number of transition lines sweep completely across the diagram for a pressure change of 10,000 kg/cm² or less. There is no apparent systematic difference in the slope of lines at the low pressure and the high pressure ends of the diagram. The different impressions given by the two sets of diagrams appears to be the result merely of the change in the scale of abscissas, and there is no significant alteration in the relative effects of temperature and pressure at high pressure. The same thing may be shown by plotting the mean slope of the various transitions lines against the mean pressure; there is no significant bunching of points in any part of the diagram.

Such a diagram does bring out, however, one significant difference between the present and the former results, namely the relative number of lines with positive and negative slopes. A negative slope, $\dfrac{d\tau}{dp}$, in itself means a state of affairs that one might be inclined to class as abnormal, for such a line means that the phase stable at higher temperature has the smaller volume. Such a state of affairs is definitely

abnormal if the two phases are liquid and solid. Only three examples of falling melting lines have been examined, water, bismuth, and gallium; in each of these cases the line falls over only a limited pressure range. Beyond that range the modification of the solid stable at low pressures is replaced by a new high pressure form, with smaller volume than the liquid, and the melting curve rises as is normal. One might perhaps anticipate the same situation for solid-solid transitions. Previous work to 12,000 had disclosed an unexpectedly large number of falling transition lines. Out of 59 examples, 14, or 24% had negative slopes. Analogy with the melting curves would lead to the expectation that at higher pressures falling transition lines would give place to rising lines, or that the total percentage of falling lines would be less for a pressure range of 50,000 than for 12,000. The opposite turns out to be the case, however. In the new work there are 44 transition lines the slope of which can be established with sufficient accuracy, and of these 19, or 43%, have negative slopes. That is, as the pressure range increases the number of "abnormal" cases increases instead of decreasing. There seems to be no inherent instability in an "abnormal" relation between the volumes of *solid* phases. An abnormal volume relation means that when the transition runs from the low pressure to the high pressure phase the system absorbs energy from the surroundings both in the form of heat and of mechanical work.

A transition line must plunge into the pressure axis vertically at the absolute zero of temperature if the third law is valid. This, combined with the fact that most of the transition lines are nearly vertical in the temperature range covered above, must mean that most of the transition lines investigated above will cut the pressure axis at absolute zero. That is, pressure polymorphism at absolute zero is a comparatively common phenomenon, and there is no tendency for it to become less common as the pressure range is increased.

We next examine statistically the volume differences between the phases. For this purpose the volume changes given above in the tables should be converted into percentage changes by multiplying by the densities. We may study in the first place the relative frequency of the different magnitudes of Δv by plotting the number of examples against the logarithm of the percentage volume change. In this way a distribution curve will be found of practically constant amplitude from volume changes of 11% down to 0.8%. Below this the distribution amplitude tails off, eventually disappearing at the smallest volume change measured above, 0.04%. The interpretation

of the tailing off is without doubt that the sensitiveness of the method is not sufficient to detect the small volume changes. Since the logarithmic scale reaches indefinitely down toward small numbers the significance of this result would seem to be that one may expect polymorphism to be a more and more frequent phenomenon the more one increases the sensitiveness of the method for detecting volume changes. This constitutes the quantitative justification for a remark made earlier in this paper.

The distribution of the changes of volume may also be studied as a function of the mean pressure of the transition. Again it will be found that there is no significant bunching of points in any part of the diagram; that is, there is no tendency for the volume changes to become either smaller or larger on the average as the mean pressure of the transition increases.

A statistical study may be made of the number of phases which exist for the different substances. If the substances formerly studied are included, the following result is obtained:

Number of phases:	2	3	4	5	6	7
Number of examples:	45	13	7	0	3	1

Very roughly, the number of examples falls off geometrically as the number of phases increases arithmetically. That is, the chance that a substance will exhibit a new phase is not affected by the fact that it may already have exhibited polymorphism.

All of these considerations display polymorphism as an essentially haphazard phenomenon. Polymorphism is likely to hit a substance at any time, irrespective of whether it has already shown it or not and irrespective of the pressure, and the accompanying volume change will be selected at random in the range from zero up to something probably not much more than 10 per cent. If the volume range from which haphazard selection is made is properly expressed on a logarithmic basis, as would be suggested by our frequency analysis, this means an unlimited amount of polymorphism in the domain of small volume changes. Such is not inconsistent with other pictures. The forces which hold solids together are known to be of various kinds, such as the ionic forces in salts, van der Waals' forces in solid inert gases, exchange and electronic forces in metals, and various combinations of these. Polymorphic transitions may be recognized corresponding to one or the other of these or to changes from predominantly one to predominantly another. There would seem to be no hard and fast line of demarcation between transitions produced by a change in the predominant type of force and the finer changes due to rearrangements

of energy levels of any sort. For this reason one may expect to find polymorphism increasingly prevalent as one increases the sensitiveness of measurement. Eventually the phenomena will doubtless receive adequate theoretical explanation, but at present the complexities are so great that a statistical study such as we have made here can disclose only a haphazard situation.

We next examine the energy changes in the transitions. It is a consequence of the fact that neither the slope nor the changes of volume exhibit any systematic trend with increasing pressure that the latent heat exhibits no trend either. The difference of energy, however, does exhibit a trend. For this can be written as $\Delta E = L - p\Delta v$, and since neither L nor Δv exhibits a trend, the trend of ΔE is the same as the trend of p itself. That is, at the higher pressures more and more substances increase in internal energy on passing from the low pressure to the high pressure modification, and this increase of energy becomes on the average more and more nearly equal to the work done by the external pressure acting through the change of volume. At the absolute zero of temperature the relations are especially simple. Here there are no heating effects, and the whole system can be described in mechanical terms. The internal pressure in each phase is equal to the external pressure; the increase of internal energy is $p\Delta v$, and the mean internal pressure during the transition (defining the mean internal pressure as that quantity which multiplied by the change of volume gives the change of energy) is exactly the same as the internal pressure in the initial and the final phases. This increase of internal energy points to a rearrangement in the structure of atoms and molecules. For Schottky's theorem, written for 0° Abs., gives:

$$\Delta E_{kin} = 4p\Delta v.$$

Since Δv must be negative on passing from the low to the high pressure modification, this means that the total internal kinetic energy is less by the amount $4p|\Delta v|$ in the high pressure modification. The total internal kinetic energy comprises the contribution arising from mass motion of the atoms, and the part from the internal motions of its electrons. In general, the high pressure phase will be a phase with greater stiffness of constraints, and therefore a greater natural frequency. The kinetic energy of mass motion arising from the zero point energy $\frac{1}{2}h\nu$ will therefore in general be greater in the high pressure phase. This demands that the internal kinetic energy of electronic motion decrease by an amount numerically greater than

$4p\Delta v$. Under normal conditions this would mean an increase in size of the atoms, a result so paradoxical that one seems forced to conclude that the electrons which contribute to the change of kinetic energy cannot be associated with particular atoms.

At temperatures above 0° Abs. there seems no reason to suppose that the decrease of internal non-classical kinetic energy does not continue to be greater than $4p\Delta v$. This is materially larger than the energies in the form of latent heat concerned with the transitions. For example, in the above tables the largest latent heat is that of the II–IV transition of KCN at 20° and 20,000 kg/cm². At this transition point the term $4p\Delta v$ is nearly 12 times as great as the latent heat. That is, in the temperature range of this work and at pressures above 20,000 ordinary thermal phenomena are a comparatively minor effect superposed on the quantum phenomena which would be exhibited in their purity at 0° Abs.

Although not large compared with ionization energies, the energy $4p\Delta v$ is nevertheless quite appreciable when expressed in electronic terms. In a previous paper[13] I have calculated that at the II–III transition of bismuth at 25,000 kg/cm² the term $4p\Delta v$ amounts to 0.18 electron volts per atom.

The change of internal energy during a transition may be written .

$$\Delta E = \Delta v \left[\frac{L}{\Delta v} - p \right] = \Delta v \left[\tau \frac{dp}{d\tau} - p \right]$$

The factor $\tau \dfrac{dp}{d\tau} - p$ may be regarded as a sort of average "internal" pressure during the transition, and the term $\tau \dfrac{dp}{d\tau}$ as an average "thermal" pressure analogous to the familiar "thermal" pressure $\tau \left(\dfrac{\partial p}{\partial \tau} \right)_v$ of homogeneous phases. I believe, however, that this analysis into "internal" and "thermal" pressures can be regarded as only a formal matter, without especial significance with regard to the mechanism. For we have already seen that in 40 per cent of the cases $\dfrac{dp}{d\tau}$ is negative, which would demand a *negative* thermal pressure during the transition. This is a difficult sort of thing to visualize, particularly when the "thermal" pressures of the phases separately are doubtless positive. In fact, I very much question whether the conventional analysis into "internal" and "thermal" pressures remains profitable even for homogeneous phases at high pressures where the

internal sources of kinetic energy which may be drawn on become more important than the classical thermal sources.

In the cases above which could be measured with sufficient accuracy the energy increases on passing from the low to the high pressure modification in 78 per cent of the cases. That is, the thermal effect overbalances the mechanical work in only 22 per cent of the cases. This is in sharp contrast with the behavior on melting; in all the cases of melting studied up to 12,000 kg/cm² the thermal term overbalances the mechanical work, usually by a factor of several fold.

It remains now to comment on various specific features. By far the most extensive group of chemically related substances examined above comprises the chlorates, bromates, iodates, perchlorates and periodates of the univalent radicals Na, K, Rb, Cs, Ag, Tl, and NH₄ (the chlorate and bromate of NH₄ were omitted because of danger of explosion in ordinary handling at atmospheric pressure). My attention was attracted to this family because the seven perchlorates are known to be polymorphic at atmospheric pressure,[14] changing over from a rhombic to a cubic modification at temperatures which range from 155° to 308°. All seven cubic modifications seem to be similar in lattice structure, but the rhombic modifications of Na and Ag are different in type from the five other rhombic modifications. One or two of the easily obtained perchlorates proved to be polymorphic under pressure, and this suggested a study of the entire family. Most of the compounds were specially made by MacKay. Six of the seven perchlorates proved to be polymorphic under pressure, the potassium compound giving the only negative result. There is no apparent connection between the new high pressure modifications and the transition at atmospheric pressure, as inspection of the phase diagrams shows at once. It would be natural to expect some resemblance between the new high pressure forms. The magnitude of the volume change would seem to be the best clue to this. The caesium and silver salts show volume changes of 5.0 and 6.0 per cent respectively, so that at first it would be natural to correlate their two high pressure forms. This is highly questionable, however, when one reflects that the low pressure rhombic form of the silver compound is known to be different from that of the caesium compound. The other volume changes are distributed as follows: Na salt, 0.4% and 3.5%; Rb, 1.7%; NH₄, 0.8% and Tl, 2.2%. It is perhaps not improbable that the high pressure forms of Rb, NH₄, and Tl are analogous, but there seems no reason to think that the other high pressure forms in this group are related. This was a surprise to me in view of the close similarity of

the phenomena at atmospheric pressure. The wide prevalence of pressure polymorphism in this group must appear to be more or less of a coincidence.

Contrasted with six out of seven cases of pressure polymorphism among the perchlorates are at most eight out of the remaining twenty-four in all the other compounds of the family. This proportion is about what it is for compounds selected at random. The exuberant polymorphism exhibited by $NaClO_3$, the first compound tried, proved a false clue to the rest of the family.

Another family in which polymorphism is of frequent occurrence is the nitrates of the univalent radicals. Exploration of the phase diagrams of six of these up to 12,000 kg/cm^2 was made some time ago.[10] Three of these, Ag, Cs, and Rb are now found to yield new forms in the extended pressure range. Of these, it is not improbable that the high pressure forms of $CsNO_3$ and $RbNO_3$ are analogous, since the atmospheric forms from which the high pressure form springs is rhombic in each case, and the change of volume at the transition is small. Except for this, there does not seem to be any particular resemblance between the phase diagrams of the various nitrates. In particular, extension of the pressure range has not proved to result in supplementing previously known phase diagrams in such a way that resemblances are disclosed which were formerly concealed by too low a range of pressure. The frequent occurrence of polymorphism in the nitrates appears to be a somewhat unsystematic phenomenon, for which the clue is not yet apparent.

This sort of discussion could be considerably extended, but always to the same conclusion, namely that the phase diagrams do not exhibit the similarities which might be anticipated because of chemical similarity. The one outstanding exception is the transition from the face centered to the body centered arrangement in the halides of NH_4, Rb, and K. But even in the simple NaCl type of structure other sorts of change are possible, as shown by the obscure low pressure change of RbCl, the small transitions of AgCl and AgBr, and the complicated phase diagram of KCN, with its large volume changes. The comparative unimportance of the chemical factor in determining polymorphic change is consistent with the suggestion presented earlier in the discussion, namely that during a polymorphic change we are concerned with internal rearrangements more deep seated than those involved in the molecular phenomena of chemistry.

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